NITROGEN FOR SPRING-SOWN MALTING BARLEY

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DECLARATION

I, Iain Peter McTaggart, declare that this thesis was composed by myself, and the work described was carried out by myself, except for the instances detailed in the text and acknowledgements.

Iain McTaggart

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ABSTRACT

Field experiments were carried out to determine the effect of nitrogen on the yield, nitrogen uptake and grain nitrogen concentration of spring barley grown for malting. The effects of the rate, timing of application and the form in which the fertiliser nitrogen was applied were studied.

The form of fertiliser nitrogen applied had little effect on grain nitrogen concentrations, except under dry soil conditions, when concentrations were higher using calcium nitrate fertiliser. Calcium nitrate also improved grain yields at low fertiliser rates, but at rates nearer recommended levels there was little difference in yield between fertiliser forms. Split or late applications of fertiliser nitrogen only improved yields when applied as calcium nitrate, and then only when early applications had been followed by heavy rain.

At low fertiliser rates, the efficiency of recovery of fertiliser nitrogen (^{15}N) in plant shoots was greater, when applied as calcium nitrate than when applied as ammonium sulphate or ammonium nitrate. Efficiency of recovery fell at higher rates in calcium nitrate treatments, but rose in ammonium sulphate treatments. Under the dry soil conditions in 1989, the efficiency of recovery was significantly increased in all fertiliser treatments. Uptake of fertiliser nitrogen was rapid in the calcium nitrate and ammonium nitrate treatments, usually reaching a maximum by anthesis. There was evidence of losses, between anthesis and harvest, of fertiliser nitrogen previously taken up by the crop. The uptake of soil nitrogen in the calcium nitrate treatments remained constant over the range of rates and timings of fertiliser application. There was evidence of increasing uptake of soil nitrogen with increased rates of ammonium sulphate fertiliser at several sites, possibly due to 'pool substitution' of ^{15}N-labelled fertiliser. Uptake of soil nitrogen was less rapid than fertiliser nitrogen before anthesis, but continued right up to harvest in most treatments. This appeared related to calculated rates of gross mineralisation, which increased during the growing season.

The most significant factor in determining total nitrogen uptake in the crop was the soil on which the barley was grown, rather than any of the fertiliser management treatments studied. Soil nitrogen uptake was significantly more variable between sites than fertiliser nitrogen uptake, despite the similar cropping histories at most sites. The variation in soil nitrogen uptake was derived mainly from differences in the mineralisation of soil organic matter over the growing season, rather than from the amount of mineral nitrogen in the soil at sowing.

Good correlations were found on all ADAS N-Index zero soils, between soil nitrogen taken up in the plant and values obtained using potassium chloride extraction techniques for measuring potentially mineralisable nitrogen. Further work is required to validate this relationship over a wider range of soils, and also to determine whether the relationship will hold for earlier sampling, which would be necessary if the technique was to become widely used.

CONTENTS

1: INTRODUCTION

Most barley used for malting in Britain is home-grown, due to the more favourable climate which, generally, does not experience the very hot and dry summers of continental Europe. Within Britain, the cooler Scottish climate with longer daylengths can also improve quality in terms of grain weight and uniform size (Ellis and Kirby, 1980). Spring barley is the major cereal crop in Scotland and in 1987 accounted for 54 % of all cereals with an annual yield in excess of 1 million tonnes (Entwistle and Crabtree, 1988). Over 90 % of this spring barley was sown to malting varieties. Barley sold for malting receives on average £20/tonne more than barley sold for feed. In years with poor harvests this premium can rise even higher. Therefore there is a strong incentive for a farmer to grow a crop of malting quality. The quality requirements for malting barley are high. The crop should have a large uniform grain size and a high germination rate. Grain nitrogen is also a very important factor in determining the malting quality of a crop. The nitrogen content of the grain should be no more than 1.7 % if the crop is likely to be accepted as of malting quality. This requires a fine balance to be struck in terms of fertiliser nitrogen applications which will produce an acceptable yield and also satisfy the maltsters' requirements for quality.

Typically, Scottish soils are characterised by low ambient temperatures and low soil moisture deficits. These conditions will have an effect on nitrogen mineralisation-immobilisation turnover in the soil, and thus the likely release of soil nitrogen and availability of fertiliser nitrogen for plant uptake. This research project studied the effect of nitrogen on the yield and grain nitrogen concentration of spring barley grown for malting under the typical environmental conditions of eastern Scotland. Knowledge of the likely release of nitrogen into the soil mineral nitrogen pool is important when deciding on the correct fertiliser rates for malting barley. The desire for optimum yields with the necessity of low grain nitrogen contents make fertiliser recommendations very important. Present advice for this area is to grow malting barley on soils of low organic matter, preferably after several years of cereals which reduce the levels of residual nitrogen (Scottish Agricultural Colleges (SAC), 1978).

Recommended fertiliser rates are approximately 120 kg N/ha on soils that have been cropped with successive cereal crops, and a lower rate of 100 kg N/ha in the first year after crops such as peas, beans or potatoes.

The main objectives of this research were to study the effects of inputs of nitrogen fertiliser on the nitrogen uptake and grain nitrogen content of spring barley, and to assess how nitrogen fertiliser management could improve the reliability of good grain quality, whilst also maintaining or improving yields. In particular the effects of rate, timing of application and the form in which the fertiliser nitrogen was applied were studied. The relative contributions of fertiliser and soil nitrogen to nitrogen uptake throughout the growing season were determined by means of ^{15}N-labelled fertiliser. Research was also carried out to assess two simple chemical extraction techniques used to determine the potentially mineralisable native soil nitrogen and its likely uptake into the crop, knowledge of which could be used to improve fertiliser predictions.

2: LITERATURE REVIEW

2.1: Malting Barley

2.1.1: Importance of spring barley in Scotland

The major cereal growing regions in Scotland range from the coastal regions of Lothian and the lowland areas of the Borders, up the eastern side of the country and along the coastal regions of the Moray and Dornoch Firths (Figure 2.1). This is generally low-lying land predominantly containing soils of grades 1-3, and with a drier climate than further west. This enables earlier sowing and better harvesting conditions, which are important in terms of yield and grain quality. Barley is the most widely grown cereal in these areas (Table 2.1).

Table 2.1: Percentage of the total arable area of the major cereal growing regions of Scotland (1987).

Crop	North	Central	South
Spring barley	57.0	58.4	44.8
Winter barley	16.0	9.3	22.1
Winter wheat	16.4	19.3	28.9

(Entwistle and Crabtree, 1988)

The reason for this dominance is a combination of climate and crop development (Lockhart, 1989). In Scotland the cooler, wetter climate means a longer growing season and later harvest than in other parts of Britain. Barley ripens earlier than wheat, enabling an earlier harvest which allows the farmer more time to get the harvest in, and to prepare for autumn sowing before conditions deteriorate. Even in the southern regions, including Lothian and the Borders, wheat only accounts for 29 % of the area of cereals grown and this value falls further north.

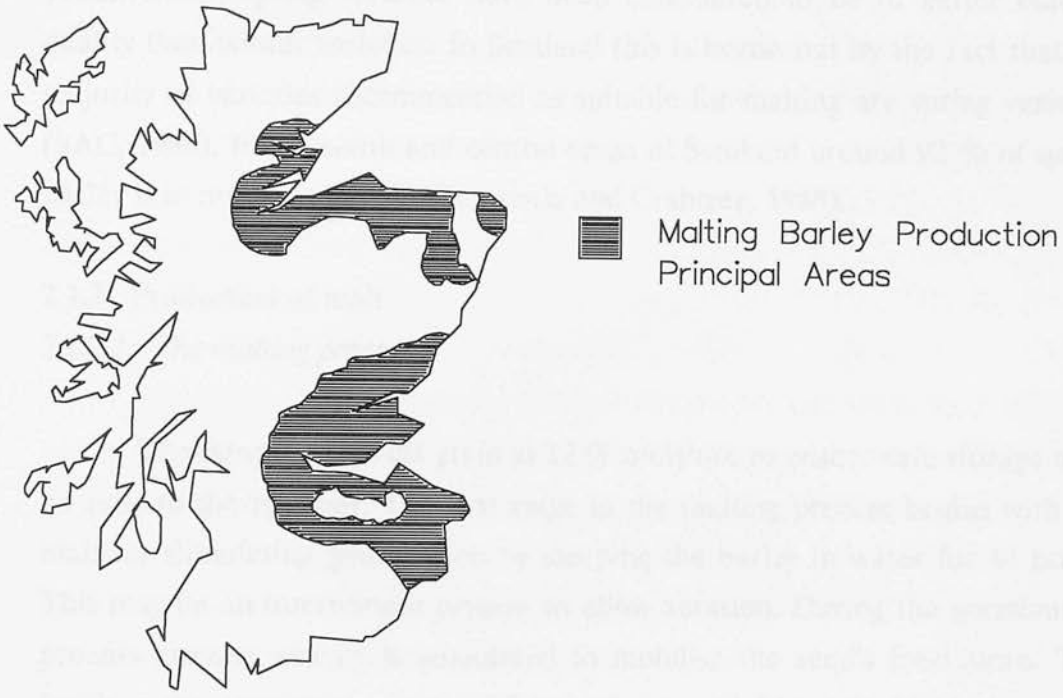


Figure 2.1: Principal areas of malting barley production in Scotland 1987 (Entwhistle and Crabtree, 1988).

Spring barley is much more widely grown than winter barley. There are two main reasons for this. The first is that climatic constraints mean that in some areas winter cereals are not suitable as described above. The other reason is economic. A farmer growing a barley crop of good malting quality (Section 2.1.3) will receive a premium on his crop compared with the price of barley sold as feed. This malting premium is on average 15 %, but can range above or below this in any year, depending on the national supplies of malting grain available.

Farmers will, therefore, try to ensure that their crop is of malting quality. Traditionally, spring varieties have been considered to be of better malting quality than winter varieties. In Scotland this is borne out by the fact that the majority of varieties recommended as suitable for malting are spring varieties (SAC, 1988). In the south and central areas of Scotland around 92 % of spring barley is in malting varieties (Entwistle and Crabtree, 1988).

2.1.2: Production of malt

2.1.2.1: The malting process

The farmer stores his grain at 12 % moisture to ensure safe storage until he sells to the maltster. The first stage in the malting process begins with the maltster stimulating germination by steeping the barley in water for 48 hours. This may be an intermittent process to allow aeration. During the germination process enzyme activity is stimulated to mobilise the seed's food store. This involves the conversion of insoluble starch into soluble maltose which can be extracted as malt. At this stage the seed can also use the sugar for growth and this is prevented by heating the seed in a kiln to terminate germination. The intensity of the kilning will determine whether the malt will be used for distilling (light kilning), or whether it will be used for beer production, with darker colour and fuller flavour (more intense kilning). For more detailed reviews of the processes involved in malting production see Hunter (1962) and Bathgate (1987).

2.1.2.2: Quality requirements for malting

Malting grain should have a maximum nitrogen content of 1.7 %, but a lower content is preferable. High concentrations of nitrogen will result in reduced amounts of starch in the grain which is the precursor for malt extract. More significantly, nitrogen in the form of proteins can form gels which delay the processing time when the ground malt is being mixed with water. Hazes in beer can also occur as a result of high nitrogen concentrations.

High germinative energy is important because the rate of germination is determined by the slowest grains. Variety is important in determining germination and also in producing plump uniform grains with loosely packed starch granules in the endosperm which are easily released when milled. Large grains also have a higher ratio of starch to protein. For further details see Bathgate (1987), Maule (1989) and Proudlove (1990).

2.2: Barley Growth and Yield

2.2.1: Environmental factors

Grain yield is related to the number of ears per unit area, the number of grains per ear, and the mass of the grain. Yield appears to correlate more closely with grains per unit area than with grain mass (Gallagher *et al.*, 1975; Dyson, 1977). In barley the grain number per unit area is determined during the period of growth just prior to anthesis, and therefore the environmental conditions experienced by the plant during this period will be very important in determining the yield of the crop (Gallagher *et al.* 1975; Dyson, 1977).

Generally, yields of spring barley are found to be higher in Scotland than in the south of England (Ellis and Kirby, 1980; Kirby and Ellis, 1980). However, data from Ellis and Brown (1986) show that this is not the case in every season. In Scotland sowing is later due to the cooler, wetter climate which means that the period of anthesis occurs later, towards the end of June. This is the time of longest daylength and it has been shown that irradiance is an important factor in determining grain number (Evans, 1978). Water stress is also an important factor, and it has been shown that grain numbers can be reduced by plants suffering such stress (Day *et al.*, 1978; Morgan and Riggs, 1981).

Low temperatures around anthesis can also have a beneficial effect on yields. In Scotland the lower temperatures, and longer daylength than is experienced further south, reduce intra-plant competition for assimilates, especially between grains in the ear, thus producing more uniform grain size throughout the ear (Ellis and Kirby, 1980). Such conditions also improve the survival rate of primordia initiated earlier (Russell *et al.*, 1982; Ellis and Russell,

1984). However, these conditions also prolong maturity, which could lead to more difficult harvesting conditions and a possible reduction in yield.

During the vegetative stages of spring growth it is the soil temperature which is the major determining factor (Gallagher, 1979). In the vegetative growth phase the stem apex temperature determines the rate of leaf extension, due to the location of the apical meristem, leaf meristem and the zone of leaf cell extension in this area (Peacock, 1975; Gallagher, 1979). The stem apex is below the soil surface during the early stages of growth (Hay, 1978). Even after stem extension it has been shown (in maize) that soil temperatures still exert some influence via the transpiration stream (Watts, 1972). However, Jones and Allen (1986) found no positive relationship between leaf emergence and temperature. Very low temperatures did slow spikelet initiation but the major factor regulating development was daylength. Wright and Hughes (1987) found that rates of leaf appearance and spikelet initiation were correlated with daylength at crop emergence, and also that spikelet initiation appeared to be correlated with temperature. Under controlled conditions, rates of leaf extension were found to be strongly correlated with temperature (Cao and Moss, 1989a) and daylength (Cao and Moss, 1989b). Ellis and Russell (1984) found that it was not always possible to separate the effects of temperature and daylength and in earlier work concluded that the longer photoperiod in Scotland could tend to offset the effect of lower temperatures on leaf emergence, and also on the level of primordium initiation (Ellis and Kirby, 1980).

After anthesis, during the period of grain filling, high temperatures and water stress can lead to reduced yields. Puri *et al.* (1985) showed that high solar radiation and high temperatures during maturation had a negative effect on grain yield in barley. The higher temperatures do increase the rate of photosynthesis and grain filling, but reduce the period of grain filling to a greater extent, leading to reduced grain weights (Evans *et al.*, 1975). Water stress also has the same effect of shortening the period of grain filling, and also shortening the duration of green leaf tissue for photosynthesis (Lawlor *et al.*, 1981).

2.2.2: Effect of nitrogen on yield and quality

The yield-promoting effect of nitrogen is principally due to an increased area of green photosynthetic tissue (Spiertz and Ellen, 1978; Willington and Biscoe, 1984). This increases the intercepted radiation which, in conjunction with the efficiency of energy conversion to yield products, is the main determinant of yield (Monteith, 1977). The increased area of green photosynthetic tissue is caused by an increase in the number of tillers and the size of individual leaves (Pearman *et al.*, 1977; Power and Alessi, 1978). Increased tiller production and survival lead to a greater number of ears formed (Remy and Viaux, 1982). Ears formed on later tillers tend to be shaded out in competition for light, with the result that fewer and smaller grains are formed in these ears (Langer and Liew, 1973; Power and Alessi, 1978; Conry, 1986), which is undesirable for a malting barley crop.

Gallagher *et al.* (1987) noted that the thousand-grain weights of barley were reduced as nitrogen rates were increased. The concentration of nitrogen in the grain has also been shown to rise when higher rates of nitrogen fertiliser are applied (Conry, 1986; Lord and Vaughan, 1987; Varvel and Severson, 1987). The relationship has been shown to be linear over a wide range of values of fertiliser nitrogen applied (Benzian *et al.*, 1983; Garstang, 1987; Stark and Brown, 1987). However, Gallagher *et al.* (1987) showed that significant rises in grain nitrogen concentrations only occurred at nitrogen application rates above those resulting in a yield increase. Murray and Nunn (1987), analysing data from experiments on winter wheat, showed that the linear relationship ceased at very high rates of nitrogen application with the grain nitrogen concentration reaching a peak at around 2.5 %. Splitting the application of nitrogen in winter barley produced slight increases in grain yield with very little increase in the nitrogen content of the grain. The most dramatic rise in grain nitrogen was found when all the nitrogen was applied at tillering, although this did also produce the greatest increase in grain yield (Conry, 1986).

In Scotland the recommended rate of fertiliser nitrogen for spring barley is 130 kg N/ha on fields with low nitrogen status, with a reduction to 90 kg N/ha

and 50 kg N/ha on fields with moderate and high nitrogen status, respectively (SAC, 1985). It is recommended that barley grown for malting should be restricted to fields with low or moderate nitrogen status (SAC, 1978). Split applications of fertiliser nitrogen should be applied before tillering but it is recommended to apply the fertiliser as early as possible. Research in America has shown that maximum yields with acceptable grain quality were achieved when the total nitrogen available, from fertiliser and soil sources, was about 120 kg N/ha (Ruffing *et al.*, 1980). Stark and Brown (1987) produced similar findings, with acceptable quality maintained with up to 135 kg available N/ha.

2.3: Nitrogen Uptake

2.3.1: Introduction

Nitrogen in the soil is mainly taken up in a mineral form, as NH_4-N or NO_3-N, through the plant root system. These nutrients reach the plant roots either by mass flow, or by diffusion, or both (Nye and Tinker, 1977). Once taken up, NO_3-N can either be reduced via NH_4-N to glutamate in the roots before translocation, or be translocated to the shoots as NO_3-N, and there either reduced to glutamate or stored as NO_3-N. NH_4-N in the roots is immediately converted to glutamate and then to the precursor amino acids glutamine and asparagine (Goodwin and Mercer, 1972; Haynes, 1986a; Wild *et al.*, 1987).

2.3.2: Fertiliser and soil nitrogen

2.3.2.1: Plant uptake of fertiliser nitrogen

The progressive recovery of fertiliser N and soil N in the plant follow separate patterns. The recovery in the plant at harvest of fertiliser N applied is usually between 40 % and 50 % (Smith *et al.*, 1984; Powlson *et al.*, 1986; Mary *et al.*, 1988).

Schjørring *et al.* (1989) showed that the recovery of fertiliser N in spring barley reached a maximum level at the time of anthesis. Between anthesis and harvest, however, a proportion of this fertiliser N was lost from the plant, with losses of up to 45 % of the fertiliser N taken up earlier in the season. Similar

patterns have been found by other workers with spring barley (Smith *et al.*, 1984; Nielsen and Jensen, 1986; Nielsen *et al.*, 1988), and in winter wheat (Destain *et al.*, 1989). Other work on winter wheat showed that the maximum uptake of fertiliser N occurred much earlier, only 35-40 days after application in the spring (Mary *et al.*, 1988; Recous *et al.*, 1988b). Use of ^{15}N tracer showed that this was due to a rapid depletion of the inorganic fertiliser pool. This rapid depletion was also found in spring barley crops (Nielsen and Jensen, 1986).

Neeteson *et al.* (1986) found similar results in some, but not all experiments, where up to 85 % of applied fertiliser N disappeared from the soil mineral pool within 1-2 weeks of application, and was not accounted for in the plant. However, after a period of 5 weeks the majority of this could be accounted for, either in the crop or in the soil. They concluded that locally high osmotic concentrations, occurring for a short period around the fertiliser granules, may have stimulated ionic uptake by microorganisms in the soil for osmoregulation, to prevent water loss to the more concentrated solution surrounding the granules. The re-appearance of the ^{15}N soon afterwards was due to the release of mineral N from the decomposition of the microorganisms, as part of the regular turnover in the soil. By this time the fertiliser granules would have mostly dissolved, removing the localised areas of high concentration.

Several different explanations have been given to account for the loss of nitrogen from the plant shoots between anthesis and maturity. Harper *et al.* (1987) demonstrated losses of 7 kg N/ha by ammonia volatilisation from the plant leaves. Other research has also reported gaseous losses (Wetselaar and Farquhar, 1980; O'Deen and Porter, 1986; Parton *et al.*, 1988). Farquhar *et al.* (1983) found that if the partial pressure of ammonia in the sub-stomatal cavities of leaves exceeded that in the atmosphere then ammonia would be lost through the leaves as a result of volatilisation. Schjørring *et al.* (1989) concluded that there is a build-up of ammonia pressure in the plant leaves when nitrogen is re-mobilised during grain filling. This pressure is greater when the sink capacity is small and therefore less of the mobilised nitrogen is able to enter the grain. They found that losses were greatest when yields and the harvest index were

low. Recous *et al.* (1988a) reported that losses of ^{15}N from plant shoots during grain filling were subsequently fully recovered in the soil organic N and concluded that losses were as a result of the exudation of NO_3-N through the roots.

2.3.2.2: Plant uptake of soil nitrogen

The total soil nitrogen in the crop, unlike fertiliser nitrogen, does not fall as the crop approaches maturity. It has been shown with spring barley (Schjørring *et al.*, 1989), and winter wheat (Recous *et al.*, 1988a) that uptake of soil nitrogen rises steadily during the vegetative growth period, and then remains at a fairly constant value during the grain-filling period. Smith *et al.* (1984) found that the soil nitrogen content of spring barley continued to rise until harvest. During this period it has been shown that nitrogen is lost from the plants, (see 2.3.3.1) and that these losses are assumed to apply equally to fertiliser- and soil-derived nitrogen. Therefore results indicating the maintenance of a constant or increasing amount of soil nitrogen in the crop over the grain-filling period all show that the uptake of soil nitrogen continues throughout the whole growing season. This can contribute up to 20-40 kg N/ha to the crop over the grain filling period (Smith *et al.*, 1984; Recous *et al.*, 1988a; Schjørring *et al.*, 1989).

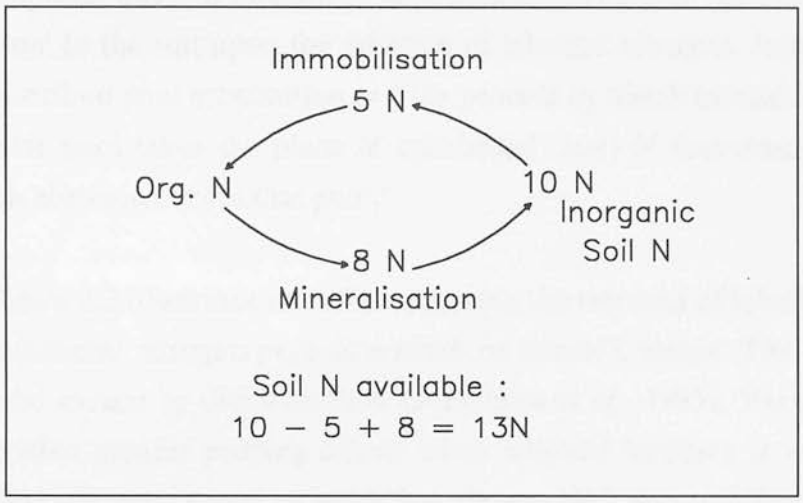
2.3.2.3: The priming effect and the interpretation of ^{15}N experiments

The 'priming effect' refers to the phenomenon where the addition of labelled nitrogen to the soil results in an increase in the amount of unlabelled nitrogen in the plant (Hauck and Bremner, 1976). Jenkinson *et al.* (1985), in a review of the processes involved and their consequences, used the term 'added nitrogen interaction' (ANI) to describe any effect that the addition of nitrogen to a soil may have on the nitrogen already present. Such effects can include a less efficient uptake of fertiliser nitrogen, when measured by isotopic ^{15}N techniques compared with non-isotopic 'difference' techniques, and also result in apparent increases in the uptake of unlabelled soil nitrogen.

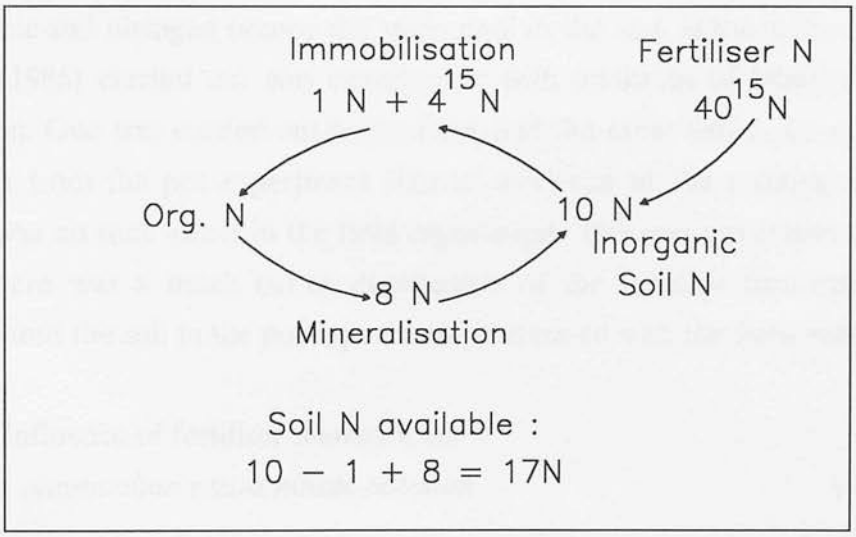
Many workers conducting research on crops with the aid of labelled fertiliser nitrogen have found that the uptake of unlabelled soil nitrogen increased with increased additions of the labelled fertiliser nitrogen (Legg and Stanford, 1967; Sapozhnikov *et al.*, 1968; Broadbent and Nakashima, 1971; Fried and Broeshart, 1974; Westerman and Kurtz, 1974; Sørensen, 1982). Equally many other workers have found no priming effect (Huntjens, 1971; Recous *et al.*, 1988a; Destain *et al.* 1989; Schjørring *et al.*, 1989). Smith *et al.* (1984) found that there was a priming effect when trials were carried out on imperfectly drained till soils in Scotland, but that there was no such effect on trials carried out on sandy soils. The different effects were attributed to more efficient root exploration at lower fertiliser nitrogen rates in the freely drained sandy soil, compared with the heavier imperfectly drained soils. Other workers have also attributed increased soil nitrogen uptake to better exploration of the soil, as a result of enhanced root growth upon the addition of fertiliser nitrogen (Aleksic *et al.*, 1968; Fried and Broeshart, 1974; Sørensen, 1982). Sapozhnikov *et al.* (1968) demonstrated this with a split-root experiment, with one half of the roots growing in soil and the other half growing in sterilised sand. When ^{15}N was added to the roots growing in the sand they found that soil nitrogen uptake via the roots in the soil increased by up to 32 %.

Other explanations put forward are that the additions of fertiliser nitrogen increase the rate of mineralisation in the soil. Suggested mechanisms for this have included osmotic changes in the soil solution upon the addition of fertiliser nitrogen salts, which could attract organic nitrogen into the soil solution where it would be more easily mineralised (Broadbent, 1970; Broadbent and Nakashima, 1971). Soil pH can be altered by the addition of fertiliser nitrogen, and this may affect microbial activities including net mineralisation (Jansson, 1971).

Another explanation is that the effects observed are not caused by any real changes in rates of mineralisation, or root growth, but are actually only apparent changes caused by the continuous mineralisation-immobilisation turnover in the soil (Figure 2.2) (Huntjens, 1971; Hauck and Bremner, 1976; Jansson and Persson, 1982; Jenkinson *et al.*, 1985). Hart *et al.* (1986) applied



Non−fertilised Crop



N−fertilised Crop

Figure 2.2: The effect of pool substitution on the amount of amount of plant available soil-N (Jensen, 1987).

small additions of highly enriched ^{15}N-labelled fertiliser, which were unlikely to be large enough to cause any real priming effect. Even so, an increase in soil nitrogen uptake was still measured, which was attributed to the effects of 'pool substitution' in the soil upon the addition of labelled nitrogen. Jenkinson *et al.* (1985) described pool substitution as " the process by which labelled N added to a particular pool takes the place of unlabelled (soil) N that would otherwise have been abstracted from that pool."

Figure 2.2 illustrates this effect, showing the removal of labelled nitrogen from the mineral nitrogen pool as a result of immobilisation. The same effect can also be caused by denitrification (Jenkinson *et al.*, 1985). Various workers have reported greater priming effects when labelled fertiliser is added in the form of NH_4-N, rather than NO_3-N (Broadbent, 1965, Sapozhnikov *et al.*, 1968, Kowalenko and Cameron, 1978, Steele *et al.*, 1980 and Mary *et al.*, 1988). This can be explained by the fact that NH_4-N is the preferred substrate for soil microbes during immobilisation (Section 2.3.3.1).

Pool substitution can only occur if the labelled fertiliser nitrogen and the inorganic soil nitrogen occupy the same pool in the soil, at the same time. Hart *et al.* (1986) carried out two experiments with additions of labelled fertiliser nitrogen. One was carried out in the field, and the other was a pot experiment. Results from the pot experiment showed evidence of the priming effect, but there was no such effect in the field experiment. This was attributed to the fact that there was a much better distribution of the labelled fertiliser nitrogen throughout the soil in the pot experiment, compared with the field experiment.

2.3.3: Influence of fertiliser management

2.3.3.1: Ammonium versus nitrate nutrition

There are two main forms in which fertiliser nitrogen can be applied: either as nitrate, in the form of compounds such as calcium nitrate or potassium nitrate, or as ammonium, in compounds such as ammonium sulphate, or as urea which is converted to ammonium in the soil. Another very common form of nitrogen fertiliser is ammonium nitrate which contains equal proportions of

both forms of nitrogen. NO_3-N is the more mobile form in the soil and therefore can be transported more quickly to the growing roots. However, this means that it is also more easily leached than NH_4-N, which can bind to negatively charged soil particles.

Experiments have shown that where there is an adequate supply of both NH_4-N and NO_3-N there is a strong preference for the uptake of NH_4-N by barley (Lewis *et al.*, 1985; Wild *et al.*, 1987), and rye-grass (Watson 1986). Temperature has also been shown to influence uptake, with a greater uptake of NH_4-N compared with NO_3-N at lower temperatures (MacDuff and Hopper, 1986).

NH_4-N can be readily converted to NO_3-N in the soil by the process of nitrification (Section 2.4.3). This process occurs in most aerated soils under conditions favourable for growing, with most of the applied NH_4-N being converted to NO_3-N over a short period of time (Haynes, 1986a). However, before the addition of NH_4-N to the soil the population of nitrifying bacteria is often small, and only rises after the ammonium addition. Hadas *et al.* (1986) have recorded delays ranging from several days to few weeks before the fertiliser NH_4-N is completely nitrified. When applying split applications of NH_4-N fertilisers it has been shown that nitrification proceeds much more rapidly after the second application (Praveen-Kumer *et al.*, 1989). This has been attributed to the fact that there is a period of several weeks after the first application during which the population of nitrifying bacteria is maintained at the higher level (Fleisher and Hagin, 1981).

Yields and total N uptake have been shown to increase in most plant species when a mixture of NH_4-N and NO_3-N is present (Schjørring, 1986; Mary *et al.*, 1988; Recous *et al.*, 1988b; Stevens and Laughlin, 1989). This is possibly because the NH_4^+ ions help to maintain the cation-anion balance in plants during nutrient absorption (Schjørring 1986). Many workers have found that the NO_3-N fraction of fertiliser nitrogen applied is recovered more efficiently than the NH_4-N fraction (Broadbent and Nakashima, 1968; Powlson *et al.*, 1986; Mary *et al.*, 1988; Recous *et al.*, 1988b).

Stevens and Laughlin (1989) found in their experiments that NH_4-N was recovered in the plant more efficiently. They suggested that the probable reason for such discrepancies was that NH_4-N fertilisers usually suffer large losses as a result of volatilisation when applied with a surface spreader. Their improved NH_4-N recovery was achieved with the fertilisers injected into the soil in solution, minimising the risk of volatilisation.

Another possible reason for poorer NH_4-N recovery is the greater mobility of NO_3^- ions moving more quickly to the plant roots, which in young plants occupy only a very small volume of soil (Greenwood and Draycott, 1988). Nielsen and Jensen (1986) found that plant uptake in spring barley was delayed with applied NH_4-N, compared with NO_3-N. Also, NH_4-N is immobilised in preference to NO_3-N, thus limiting its availability for plant uptake (Steele *et al.*, 1980; Okereke and Meints, 1985; Recous *et al.*, 1988a).

2.3.3.2: Timing of application

To maximise the efficiency of recovery of fertiliser nitrogen it should be made available to the plant as required, i.e. nitrogen applications should be split over a period of time to ensure a more adequate supply as the plant develops. The optimum time for nitrogen utilisation by the plant is at the time of most rapid uptake of N by the plant, which is at the start of stem extension (Widdowson *et al.*, 1987). Dilz and Verstraeten (1987) found that the greatest recovery of fertiliser N was from nitrogen applied at tillering. This is because the opportunity for losses is reduced by restricting the time the fertiliser is in the soil and not utilised (Olson and Kurtz, 1982). This can be very important in the Scottish climate because the relatively cold and wet conditions increase the possibility of denitrification and leaching losses.

Also, after sowing it takes time for an adequate root system to develop to utilise the available nitrogen. MacDuff *et al.* (1986) showed that rates of root extension, growth of root hairs, and overall expansion of surface area in barley increased over a temperature range of 3 ^{o}C to 25 ^{o}C. Under typical Scottish conditions soil temperatures at depths between 5 cm and 20 cm rarely rise

above 10 ^{o}C during the early part of the growing season (Hay, 1976). This would reduce the rate of root expansion, and therefore limit the ability of the crop to utilise all the available nitrogen applied at sowing. Easson (1984) found that by delaying the application of fertiliser N to spring barley N uptake was improved, but that it could also increase grain nitrogen concentrations. Later applications of fertiliser N tend to be taken up directly into the grain (Riga *et al.*, 1988; Destain *et al.*, 1989).

2.4: Nitrogen Transformations in the Soil

The mineral nitrogen that is the direct nitrogen source for all non-fixing plant species accounts for about 1 % of the total nitrogen content in the upper layers of soils (Woodmansee *et al.*, 1981). The overwhelming proportion of the nitrogen is present in the form of organic compounds. There is a continuous cycling of nitrogen within this system. Nitrogen is added to the soil via the biological fixation of atmospheric N_2 gas by N-fixing microorganisms (either free-living or in symbiotic association with plants), or by industrial fixation during fertiliser production and as a by-product of other industrial processes. Soil losses occur through leaching of mineral nitrogen, plant uptake followed by harvesting, and through denitrification (Figure 2.3).

2.4.1: Integration of soil nitrogen subcycles within the universal nitrogen cycle

The overall nitrogen cycle can be simplified by dividing it into three interdependent subcycles (Jansson, 1971; Jansson and Persson, 1982. See Figure 2.4). The elemental subcycle (E) comprises the pathways which allow nitrogen from the atmosphere to enter the soil nitrogen system, via N-fixation, and ultimately return to the atmosphere via denitrification. The autotrophic subcycle (A) comprises the incorporation of inorganic nitrogen into plants, and subsequent build up of organic substances through the process of photosynthesis, followed by eventual degradation upon death. The third subcycle, the heterotrophic subcycle (H), involves heterotrophic micro-organisms which make up the microbial biomass. It is within this subcycle that

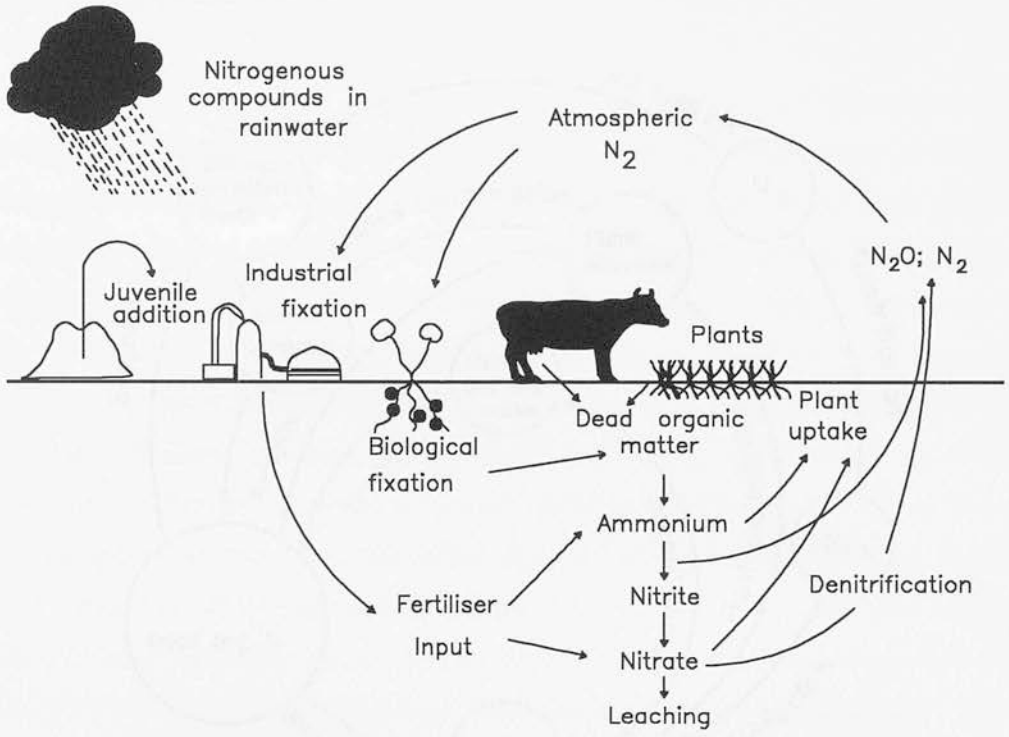


Figure 2.3: The universal N cycle (Haynes, 1986).

the processes of mineralisation and immobilisation occur. These processes, linked with the uptake, assimilation and decomposition of plants, produce a continuous turnover of nitrogen and other elements in the soil.

Immobilisation involves the assimilation and transformation of inorganic nitrogen to organic nitrogen, by soil microorganisms which incorporate it into their tissues. Mineralisation is the opposite process, involving the microbial breakdown of soil organic matter to form inorganic nitrogen, which is then available for plant uptake, or re-immobilisation, or it can be lost from the system via denitrification or leaching.

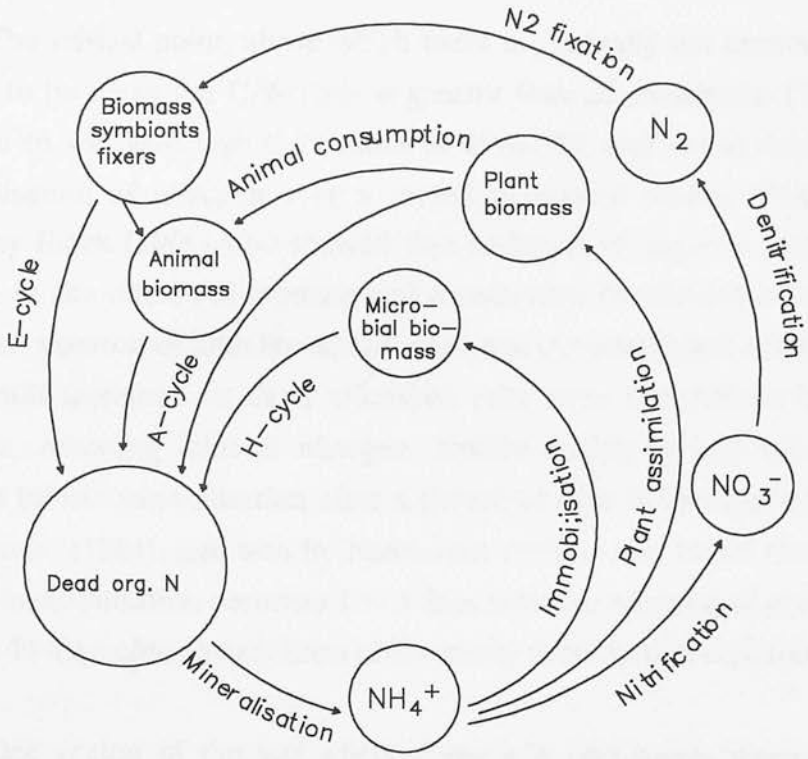


Figure 2.4: The universal N cycle divided into its three subcycles: the elemental (E), the autotrophic (A) and the heterotrophic (H) (Jansson and Persson, 1982).

2.4.2: Mineralisation-immobilisation turnover (MIT)

Both these processes are continuously working, and therefore any change in the nitrogen status in the soil will be a net effect. The major factor which determines whether there is net mineralisation or immobilisation appears to be the C/N ratio of the organic matter in the soil awaiting degradation. Material containing high C/N ratios will usually result in net immobilisation, as the microbial biomass scavenges extra mineral nitrogen to incorporate into its

tissues to utilise the extra carbon available. At such times the microbial biomass is in competition with nitrifying organisms and plants for the mineral NH_4-N, but is usually dominant, leading to reductions in the mineral nitrogen available for plants (Allison, 1973).

The critical point, above which there is generally net immobilisation, is thought to be when the C/N ratio is greater than 25. Jenkinson (1984) added substrate to soil with high C/N ratios of about 30, and found that this led to immobilisation of nitrogen over a period of several weeks. This confirmed results by Black (1968) who showed that additions of sugar to soils led to an increase in the microbial biomass and a reduction of mineral nitrogen in the soil. After a period of time the added sugar was exhausted and mineral nitrogen on the soil increased as dead microbial cells were mineralised by surviving microbes, releasing mineral nitrogen. Similar phases of net immobilisation followed by net mineralisation after a period of time were reported by Carter and Rennie, (1984), and also by Nicolardot (1988), who found that maximum rates of immobilisation occurred 1 to 3 days after the addition of glucose to soil, and 7 to 14 days after the addition of less easily decomposed cellulose.

One region of the soil where there is a continuous supply of readily available carbon is the rhizosphere, where root exudates and sloughed-off tissues are present (Warembourg and Billes, 1979; Sarkar and Wyn Jones, 1980; Newman, 1985). Generally C/N ratios in soil average 10:1 (Lambers, 1987; Robinson *et al.*, 1989), which could lead to local mineralisation around the roots (Trofymow *et al.*, 1987; Biondi *et al.*, 1988). However, whether this occurs depends on the presence of predatory bacteria in this rhizosphere (Clarholm, 1985; Ingham *et al.*, 1985; Ritz and Griffiths, 1987). Gasser *et al.* (1967) found that the addition of fertiliser nitrogen increased immobilisation even when no decomposable material was added. This observation is supported by Kitur *et al.* (1984), who found that immobilisation increased roughly in proportion to the level of fertiliser nitrogen applied. Nielsen and Jensen (1986) found that a few days after the application of NH_4NO_3 to spring barley on a sandy clay loam, 60 %-80 % of the fertiliser N was unavailable, but over the next 60 days 20 %-30 % of this "lost" nitrogen was taken up by the crop. They attributed this to the

immobilisation and subsequent re-mineralisation of fertiliser ^{15}N. Nicolardot (1988) found that 30 %-40 % of newly immobilised nitrogen was re-mineralised during the first 12 weeks of an incubation experiment. Dowdell and Webster (1984) found that freshly immobilised fertiliser N was generally re-mineralised at a rate of 10 % per year.

This phenomenon was first reported by Jansson (1958) who described the process as the "continuous internal cycle". He postulated that there is a mineralisation-immobilisation turnover which repeats itself continuously until any added material is exhausted. This is as a result of the constant turnover of the soil microbial biomass (Jenkinson and Ladd, 1981; Juma and Paul, 1984) contributing substantial amounts of nitrogen to the pool of available nitrogen in the soil (Anderson and Domsch, 1980; Paul, 1984). Microbial cells have a higher nitrogen content (5 %-10 %) than plant cells, with much of this in the form of proteins (Parsons and Tinsley, 1975). It has been shown that much of the readily mineralisable nitrogen comes from amino-acid and amino-sugar fractions (Isirimah and Keeney, 1973; Powlson, 1980; Singh *et al.*, 1981). Upon immobilisation of mineral nitrogen, most of this nitrogen is found in similar fractions (Broadbent, 1968; Ladd and Paul, 1973; Smith *et al.*, 1978; Shen *et al.*, 1984; Kelley and Stevenson, 1985; Nicolardot, 1988).

2.4.3: Effect of environmental conditions

Temperature is very important because of the role it plays in regulating the activity of the microorganisms in the soil. Near freezing point, their activity is very low. Addiscott (1983) found that mineralisation and nitrification had similar sensitivities to temperatures, with activity decreasing sharply below 5 ^{o}C. Stanford *et al.* (1973a) showed that over a range of 5 ^{o}C to 35 ^{o}C the rate of mineralisation was increased, with a temperature Q_{10} of 2. In field conditions, Nishio and Fujimoto (1989) showed that rates of mineralisation increased with increasing temperatures during the growing season. The only exception occurred in June when decreased mineralisation was attributed to very low soil moisture contents. This strong interaction between temperature and moisture in the soil has also been demonstrated by Cassman and Munns (1980). Stanford *et*

al. (1973b; 1975) found that fluctuating temperatures had no effect on rates of mineralisation. However, Biederbeck and Campbell (1973) found that rates of mineralisation were dependent on the previous temperature. Low temperatures increased the deaths of microorganisms which resulted in a flush of mineralised nitrogen as the surviving microbial population digested the newly available substrate. They showed that the first cold spell in autumn, and any late spring frosts, would produce sudden flushes of nitrate production, due to the deaths of significant fractions of the large microbial population which had built up during the previous periods of warmer temperatures.

Stanford and Epstein (1974) showed that mineralisation increases with increased moisture content up to an optimum around 30 % moisture content. Moisture stress inhibits microbial growth, and at higher moisture contents soil aeration decreases. Under these conditions mineralisation is restricted to anaerobic organisms which are less common than aerobic organisms. They are also less efficient convertors of nitrogen, leading to greatly reduced mineralisation (Campbell, 1978; Patrick, 1982). Fluctuating moisture contents, which result in the drying and rewetting of soils, stimulates mineralisation in the form of nitrogen flushes. This is thought to be due to the accumulation of dead microbial cells during a dry period, which serve as a nitrogen-rich substrate for the surviving microbial population following rewetting (Campbell and Biederbeck, 1982).

2.4.4: Nitrification

Nitrification is the process whereby NH_4^+ is oxidised to NO_3^- via NO_2^-, and occurs in virtually all soils where conditions are favourable and there is a supply of NH_4^+ substrate.

Generally, under well drained soil conditions available NH_4^+ is rapidly transformed to NO_3^- over a short period of time (Haynes, 1986a). Recous *et al.* (1988a) showed that under low temperatures, in early spring, nitrification of applied nitrogen was complete after 35 days. The optimum temperatures for nitrification are between 25 ^oC and 35 ^oC (Kowalenko and Cameron, 1976).

However, optima can vary with climate; Malhi and McGill (1982) found that soils from central Alberta, in Canada, had an optimum temperature of 20 ^{o}C, and an upper limit of 30 ^{o}C. Addiscott (1983) found that in Britain nitrification activity virtually ceased below 5 ^{o}C. As mentioned above with respect to mineralisation, wetting and drying and freezing and thawing soils increases nitrification (Biederbeck and Campbell, 1973). This increase is due to the sudden availability of NH_4-N as a result of the increased mineralisation.

Shaviv (1988) and Nishio and Fujimoto (1989) showed that nitrification rates can be inhibited when large concentrations of NH_4-N are applied to soils. This was suggested as a possible mechanism for preventing rapid accumulation of NO_3^- in the soil leading to possible losses before plant uptake. This effect could possibly be due to a lowering of the pH, if fertiliser is applied as $(NH_4)_2SO_4$ (Malhi and McGill, 1982), or due to an increase in the salt content of the soil increasing osmotic pressure (Laura, 1977; Malhi and McGill, 1982; Darrah *et al.*, 1986).

2.5: Prediction of the Fertiliser Nitrogen Requirement

2.5.1: Fertiliser recommendation systems

There is a wide variety of methods used in different countries to obtain fertiliser recommendations. All of them, however, could be described to varying degrees in terms of a balance sheet approach (Sylvester-Bradley *et al.*, 1987). In France, a simple equation balancing expected nitrogen yield of the crop with residual and mineralised soil nitrogen supply, taking into account the efficiency of uptake of fertiliser nitrogen, is used to predict optimum fertiliser rates (Viaux, 1984). Similar methods are widely used in areas of the U.S.A. (Myers, 1984). In Germany and Holland more emphasis is placed on amounts of residual nitrogen in the soil profile in the spring (Becker and Aufhammer, 1982; Ris *et al.*, 1981). In the U.K., fertiliser recommendations are made using the N-Index system (MAFF, 1985; SAC, 1985). This system is based on past cropping to determine the likely nitrogen supply from the soil.

Measurements of mineralisable nitrogen by means of incubation methods have been carried out on numerous occasions, but to date they have only been employed as indicators of fertiliser nitrogen requirements in one or two mid-west states in the U.S.A. where the climate and soils are relatively uniform (Keeney, 1982b).

The use of computer models which quantitatively simulate nitrogen turnover and crop N uptake have also been suggested as possible methods for fertiliser prediction (Addiscott and Whitmore, 1987: Addiscott *et al.*, 1991; Kersebaum and Richter, 1991).

2.5.2: Assessment of soil nitrogen supply

2.5.2.1: Residual mineral nitrogen

Measurements of residual mineral nitrogen in the soil profile are important in areas where leaching losses are likely to be small. Predictions based on residual nitrogen measurements are used in Germany (Becker and Aufhammer, 1982; Wehrmann *et al.*, 1987) and in the Netherlands (Ris *et al.*, 1981). Wehrmann *et al.* (1987) showed that improved fertiliser efficiency could be obtained by measuring the residual nitrogen in the soil in the spring, and calculating the required fertiliser nitrogen from this. However, they also required to know the amount of mineralisable nitrogen available during the growing season (calculated by empirical methods based on previous cropping, previous fertiliser applications and the optimum crop requirement for nitrogen from the results of fertiliser trials). Neeteson and Zwetsloot (1989) recommended that soil type and previous organic manure applications should be taken into account when predicting fertiliser nitrogen applications on the basis of residual nitrogen measured in the spring. Dilz (1981) found that measurement of residual nitrogen in the spring did not improve recommendations for spring barley on light sandy soils, compared with a fixed fertiliser rate applied to all sites. Ammonium-N should be measured as well as nitrate-N, as the amounts could be important (Needham, 1982).

Depth of sampling is very important in determining the total available nitrogen for the crop. The rooting depths of crops are important in determining the depth of sampling required to assess the available nitrogen (Soper *et al.*, 1971; Ludwick *et al.*, 1977). The rooting depth can be as great as 150-180 cm in crops such as wheat and maize (Herron *et al.* 1971; Daigger and Sander, 1976). Practically, however, it would be very useful to find a good relationship between nitrogen uptake and residual nitrogen in the soil, by sampling to a much shallower depth (Smith, 1977). Soper *et al.* (1971) found a good relationship between the uptake of nitrogen in barley and residual nitrogen in western Canada, sampling to a depth of 60 cm, and this is now the recommended sampling depth. In Germany samples are taken to a depth of 90 cm for winter wheat (Wehrmann *et al.*, 1987), and in the Netherlands good correlations were found with winter wheat and mineral nitrogen to 100 cm depth (Ris *et al.*, 1981).

2.5.2.2: Previous cropping

Previous cropping in a soil can influence the soil nitrogen available for crop uptake. The N-Index system for predicting fertiliser requirements in the U.K. is based on previous cropping (MAFF, 1985; SAC, 1985). The system classifies the nitrogen status of soils into 3 categories (low, medium and high) on the basis of previous cropping. This is calculated on the basis of the number of years of grass in the rotation and the last crop grown. Generally, soils which have been in cereals are categorised as having low nitrogen status, and have higher fertiliser nitrogen recommendations than moderate status soils which have been in legumes. Concentrations of nitrogen in the grain have been shown to be higher after break crops (peas, beans, oil seed rape) than after another cereal (Batey and Reynish, 1976). However, Vaidyanathan *et al.* (1987) found that there was no difference in grain nitrogen concentration in crops following a cereal or a break crop. They found that increases in yield following a break crop accounted for the greater uptake of soil nitrogen, rather than producing grain with higher nitrogen concentrations. Similar prediction methods are used in some states in the U.S.A. (Keeney, 1982b; Olson and Kurtz, 1982).

2.5.2.3: Estimation of potentially mineralisable nitrogen

In most of the recommended fertiliser nitrogen advice systems mentioned above, the component of mineralisable nitrogen taken up by the crop during the growing season was either ignored, or estimated on a subjective basis. There have been many attempts to obtain a direct measurement of the likely release of nitrogen from a given soil by a wide variety of methods, but to date no methods have been included in recommendation systems because of either, the time and effort required to obtain the necessary data, or the unreliability of the results.

(i): Biological incubation methods

Biological incubation methods usually involve the measurement of mineral nitrogen in a soil sample, before and after incubation, over a period of a few weeks.

a. Aerobic incubations. Keeney and Bremner (1967) determined the amount of NH_4-N, NO_3-N, and NO_2-N produced by 10 g of soil mixed with 30 g of washed sand and incubated at 30 ^oC for 14 days. A major difficulty with aerobic incubations is the control of the moisture content of the soil. This was overcome in the above technique by adding a constant level of water to the soil-sand mixture. Good correlations were found between mineralised nitrogen and the uptake of nitrogen by the crop. These results have been validated by other workers (Ryan *et al.*, 1971; Baerug *et al.*, 1973).

However, over such a short incubation period it has been shown that results from aerobic incubations can be influenced by the handling and pretreatment procedures in different laboratories (Bremner, 1965), and also that mineralisation can be significantly affected by the decomposition of recently incorporated crop residues (Stanford *et al.*, 1974). Over a short period the rapid decomposition of such residues can exaggerate the actual long-term mineralisation potential of a soil.

To overcome these factors Stanford and Smith (1972) devised an aerobic incubation procedure lasting 30-40 weeks. In this procedure a soil sample was mixed with washed sand and placed in a leaching tube plugged with glass-wool. At the start of the experiment initial mineral nitrogen was leached out with 0.01M $CaCl_2$, the soil was then given 25 ml of N-free nutrient solution, and the soil maintained at the correct moisture content by suction. Mineral nitrogen produced during the incubation was periodically leached out, and the soil then re-adjusted for nutrition and moisture content as described for the start of the experiment. The nitrogen mineralisation potential of the soil was estimated from the cumulative amount of nitrogen mineralised over the incubation period, based on the assumption that the nitrogen mineralised obeys first-order kinetics; i.e. that the rate of mineralisation is proportional to the amount of potentially mineralisable nitrogen:

$$\log (N_o - N_t) = \log N_o - k_t/2.303$$

where N_t = N mineralised at time t (mg kg^{-1} cumulative);
t = time (weeks);
k = the mineralisation rate constant;
N_o = N mineralisation potential (mg kg^{-1}).

This value of N_o could be considered as a definable soil characteristic indicating the possible nitrogen mineralisation of a soil under optimum conditions. It could also be used to provide a common basis for comparing various biological and chemical assessments of available nitrogen. However, Smith *et al.* (1980) found that the periodic leaching to measure inorganic nitrogen produced in this type of incubation also removed organic nitrogen, which reduced the available mineralisable substrate. This could significantly affect the mineralisation potential and the mineralisation rate constant. In all aerobic incubation techniques it is important that all forms of inorganic nitrogen (NH_4-N, NO_3-N and NO_2-N) are measured, because nitrification of NH_4^+ to NO_3^- may not be complete in all soils (Vlassak, 1970; Gasser and Kalembasa, 1976). The major drawback with all these methods is that they are impractical for regular use in soil testing laboratories. Analysis is time-

consuming, the process is slow, taking from 2 weeks to 30 weeks, and also a lot of space is required to store the incubating soils at the correct temperature.

b. Anaerobic incubations. This type of incubation has been examined because it is much simpler to carry out than aerobic incubations. There is no need to maintain the correct soil moisture content, NH_4-N only need be measured because there is no nitrification under anaerobic conditions, and there is more rapid mineralisation allowing shorter periods of incubation (Keeney, 1982b).

Waring and Bremner (1964) devised a technique which involved placing 10 g of soil in a sealed cylinder containing 25 ml distilled water, and incubating at 30 ^{o}C for 7 days. At the end of this period the soil plus the extract was steam-distilled to determine available NH_4-N. In a modification of this technique, Keeney and Bremner (1966) found that incubations for 7 days at 40 ^{o}C were better correlated with nitrogen uptake by rye-grass than 14-day incubations at 30 ^{o}C. Higher temperatures increase the rate of mineralisation. Other workers have also found good correlations between nitrogen mineralised in anaerobic incubations and nitrogen uptake by plants in greenhouse studies (Gasser and Kalembasa, 1976; Giest, 1977; Powers, 1980; Stalk and Clapp, 1980). Smith and Stanford (1971) found that amounts of NH_4-N released from anaerobic incubations were very similar to the total NH_4-N, NO_3-N and NO_2-N released from aerobic incubations, over a wide range of agricultural soils. However, Baerug *et al.* (1973) found poorer correlations using anaerobic incubations, compared with aerobic incubations.

(ii): Chemical Extraction Methods

Although not simulating the microbial activity which mineralises soil nitrogen, chemical extraction methods for estimating potentially available mineral nitrogen have been devised because they are much more rapid, and more convenient than biological incubations. Chemical extraction techniques can be categorised into three broad groupings based on the intensity of the oxidation reaction involved.

a. Intensive extraction techniques. These methods use strong extracting solutions which remove a substantial proportion of the total soil nitrogen. Keeney and Bremner (1966a) refluxed soils in 6 M HCl for 12 hours, removing about 75 % of total soil nitrogen and obtaining values that correlated well with the values for total soil nitrogen. Similar correlations were found by Giest and Hazard (1975), who extracted about 20 % of total soil nitrogen by boiling the soil with 4.5 M NaOH. These extractants remove completely the fractions of soil organic nitrogen which are susceptible to mineralisation (Stanford, 1968a). However, such amounts are much greater than could have been mineralised in a soil under normal conditions, and these intensive extraction techniques are generally found to be no better at estimating nitrogen availability than standard techniques for measuring soil organic matter (Stanford, 1982).

b. Intermediate extraction techniques. Extractants such as alkaline $KMnO_4$ and NaOH (0.125-0.625 M) yield smaller amounts of NH_4-N than the intensive extractants, but correlations with biological indexes of nitrogen availability are still not very reliable (Keeney and Bremner, 1966b; Jenkinson, 1968; Stanford, 1978). Extractions using dilute acids, such as H_2SO_4, have been studied by various workers (Smith, 1966; Cornforth, 1968; Stanford, 1978), but correlations with biological availability indexes are still not very strong. A possible reason for this is that even these relatively mild acid extractants still remove substantial proportions of relatively inert, biologically resistant organic fractions (Stanford, 1982).

c. Mild extraction techniques. Mild extractants, such as dilute HCl or $Ba(OH)_2$, derived a substantially greater proportion of extracted nitrogen from the biologically active pool than the more severe extractants (Jenkinson, 1968).

Stanford and Smith (1976) found a relatively good correlation between NH_4-N distilled after autoclaving a wide range of soils in 0.01 M $CaCl_2$ for 16 hours, and mineralisable nitrogen measured by biological incubation. Stanford (1968b) and Stanford and DeMar (1970) fractionated the nitrogen present in extracts obtained from boiling soils in 0.01 M $CaCl_2$ for 16 hours, and autoclaving soils for 16 hours in the same extractant, respectively. They found

that distilled NH_4-N correlated better with mineralisable nitrogen than did amino-N, unidentified nitrogen, or total nitrogen present. The temperature and duration of the extraction procedure also affects the amount of nitrogen extracted. Stanford and Smith (1976) found that autoclaving a wide range of soils for 16 hours in 0.01 M $CaCl_2$ consistently released about 2.5 times the amount of nitrogen released by boiling for 16 hours with the same extractant.

More recently, workers have devised techniques based on KCl extracting solutions of differing concentrations over various periods of time (Oien and Selmer-Olsen, 1980; Whitehead, 1981; Gianello and Bremner, 1986a). Oien and Selmer-Olsen (1980) extracted with a 2M KCl solution at 80 ^oC for 20 hours. Very good correlations were found between extracted nitrogen and that released by aerobic incubation. Whitehead (1981) also found good correlations, between nitrogen released and nitrogen uptake by rye-grass, over a range of 23 soils when they were boiled with 1M KCl for 1 hour. Smith and Li (1984) used a modification of the Whitehead method. This involved boiling the soil solution in a beaker covered with a watch glass to prevent the loss of NH_3 during boiling. With the exception of one anomalous soil, correlations between total nitrogen extracted and nitrogen uptake by rye-grass, oats and barley were high.

Gianello and Bremner (1986b) compared a wide range of chemical extraction procedures with a series of accepted biological incubation techniques, to evaluate two new chemical extraction methods over a range of 30 different soils. The first method involves boiling 3 g of soil in 20 ml 2 M KCl at 100 ^oC for 4 hours in a stoppered boiling tube, and measuring the NH_4-N extracted. The second method involves steam-distilling 4 g of soil with 40 ml of phosphate-borate buffer (pH 11.2) for 8 minutes, and measuring the NH_4-N liberated. Correlations between the nitrogen extracted by the two techniques and the nitrogen mineralisation indexes from the biological incubations were high, accounting for approximately 90 % of the variation in the nitrogen mineralisation potential of the soils measured.

Results from the Øien and Selmer-Olsen (1980) method were also obtained for the same soils, and showed that the correlations from this method

were similar to the Gianello and Bremner methods. However, considering the 20 hour heating period, and the fact that there is an extra filtration step in the Øien and Selmer-Olsen method, it was considered that it was much less convenient to carry out routinely. Results from the extractions carried out with the Whitehead (1981) method showed that the correlations were not as good as found with the other KCl extractions. A modification, similar to that carried out by Smith and Li (1984), was also carried out. This time the sample was heated in a stoppered tube at 100 ^{o}C to prevent NH_3 loss, and the extracted NH_4-N then measured. Extracted NH_4-N increased under this modification, and this resulted in better correlations with the nitrogen mineralisation indexes from the biological incubations (Gianello and Bremner, 1986b).

2.5.2.4: Computer simulation of fertiliser nitrogen requirement

Recently, research has been carried out with the aim of producing a simple model which will predict the fertiliser nitrogen requirement of crops from the input of information which is easily obtainable. Addiscott and Whitmore (1987) developed a model which simulated various components of the soil nitrogen turnover processes including leaching, mineralisation of soil organic matter and also growth and nitrogen uptake in the crop, which was winter wheat. This model was further developed (Addiscott *et al.*, 1991) for management and advisory purposes requiring the input of information readily available to the farmer and the advisor. Simulations of the fate of mineral nitrogen in the soil and crop over the winter and early spring correlated well with field results. However, the model was less successful in simulating the fate of spring applied fertiliser nitrogen either in the soil or in the crop. This appeared to be due to a short-term fixation or immobilisation of applied nitrogen with some reappearance a few weeks later. Other research has encountered similar problems. Kersebaum and Richter (1991) developed a model for advisory purposes in Germany and also found that poor simulations occurred immediately after the application of spring fertiliser nitrogen. Again the cause appeared to be the rapid and temporary disappearance of applied nitrogen which was not properly accounted for in the model. This was attributed in part to microbial immobilisation, but could not account for all of the losses.

Myers (1984) produced good simulations of the predicted fertiliser nitrogen requirement when the rates to be applied were either very low or very high, but was less successful in accurately predicting moderate fertiliser requirements. Van Keulen and Stol (1991) concluded that at present there is insufficient quantitative knowledge of the rates of the basic processes involved in nitrogen turnover in the soil and crop nitrogen uptake. Therefore present models appear inadequate for accurate fertiliser predictions, but are important in highlighting the most important factors wich require further research.

2.5.2.5: Direct measurement of mineralisable nitrogen

Gross mineralisation and immobilisation can be calculated using nitrogen isotope dilution techniques. Kirkham and Bartholomew (1954) derived equations for calculating gross transformation rates in soils based on the dilution of added $^{15}NH_4$-N and $^{15}NO_3$-N with unlabelled soil nitrogen. More recently another method has been developed (Barraclough and Smith, 1987; Barraclough, 1988). This method uses duplicate applications of $^{15}NH_4{}^{14}NO_3$ and $^{14}NH_4{}^{15}NO_3$ to microplots enabling the fate of both forms to be followed, and using simultaneous equations allows gross rates of mineralisation, immobilisation and nitrification to be calculated. A description of the theory and the derivation of the equations used in the calculations are given below. A number of assumptions were used in the derivation of the following equations.

1. The time interval was selected such that all processes could reasonably be represented as zero order.
2. No preferential exploitation of ^{15}N or ^{14}N occurred. Both were consumed in proportion to their relative amounts.
3. Nitrogen mineralised from the soil organic matter has a ^{15}N abundance of 0.366 atom %.

Using these assumptions the following equation relates $[\mathbf{(N15')_t}]$ the ^{15}N excess abundance of the $^{15}NH_4$-labelled pool at time t, to (**M**) the rate of mineralisation, (**t**) time expired, ($\mathbf{C_0}$) the size of the ammonium pool after fertiliser addition, (ø) the rate of change of the ammonium pool size, and $[\mathbf{(N15')_0}]$ ^{15}N excess abundance of the ammonium pool just fertiliser addition.

$$(N15')_t = (N15')_0 / (1 + \phi t/C_0)^{M/\phi} \qquad (1)$$

This equation gives a value for the rate of mineralisation using values from the $^{15}NH_4$-labelled microplot. The same equation can also describe the ^{15}N abundance of the nitrate pool in the $^{15}NO_3$-labelled microplot receiving unlabelled N from the ammonium pool via nitrification. The rate of nitrification (N) can be calculated from the same equation, substituting N for M, where the symbols have the same meaning as those in equation (1), but now refer to the nitrate pool.

$$(N15')_t = (N15')_0 / (1 + \phi t/C_0)^{N/\phi} \qquad (2)$$

Knowing the nitrification rate (N), or the mineralisation rate (M), it is possible to calculate (**Y**), the mean pool ^{15}N of the relevant pool over the period of the experiment. For example, to calculate the mean pool ^{15}N in the $^{15}NH_4$-labelled microplot:

$$Y = \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} 0.00366t + \frac{C_o^{M/\phi} \left(\frac{C_1}{C_o} - 0.00366 \right) (C_o + \phi t)^{(1 - M/\phi)}}{(\phi - M)} \qquad (3)$$

C_i is the size of the ammonium pool at time = t,

and the value 0.00366 is derived from the assumption that nitrogen mineralised from the soil organic matter has a nitrogen abundance of 0.366 atom %.

The proportion of N in the crop recovered from the nitrate pool (R_N) is then given by:

$$(R_N) = (X-0.366)/(Y-0.366) \times 100\ \% \qquad (4)$$

where X is the ^{15}N content in the crop at time = t.

By difference, the recovery from the ammonium pool (excluding that taken up as nitrate following nitrification) can be calculated. The rate of decline in the ammonium pool size (ø in equation (1)) can also be calculated as follows:

$$ø = M - I - N - U \qquad (5)$$

where I is the rate of immobilisation, and U is the rate of uptake from the ammonium pool by the plant.

$$U = (\text{plant N at } t_t - \text{plant N at } t_0) \times \%\ \text{recovery from } NH_4 \text{ pool} \qquad (6)$$

By re-arranging equation (5) the rate of immobilisation can be calculated.

$$I = M - N - U - ø \qquad (7)$$

3: SITES, MATERIALS AND METHODS

Field trials were carried out with spring barley, on a range of sites in eastern Scotland, over four years from 1987.

3.1: 1987-1989 Seasons

3.1.1: Site preparation and fertiliser application

Two sites were selected in each of the three years 1987-1989 to study the effects of rate, form and timing of nitrogen fertiliser applied to spring barley grown for malting. Details of these sites are given in Table 3.1. All of these sites were located within larger main trial sites managed by the Crop Production and Advisory Department (CPAD) of the East of Scotland College of Agriculture (now SAC). Members of CPAD were responsible for the preparation, application of basal rates of P and K fertiliser, sowing and general management of the trial plots. Their assistance is gratefully acknowledged.

The trials involved three forms of nitrogen fertiliser, each applied at several different rates and timings (Table 3.2). The three forms of fertiliser compared contained (a) all the nitrogen in the nitrate form (as calcium nitrate), (b) all the nitrogen in the ammonium form (as ammonium sulphate), and (c) equal proportions of ammonium and nitrate (as ammonium nitrate). The field experiments were laid out in a split-plot design. The main treatment plots contained the rate and timing of fertiliser application, which were laid out in a randomised block design of three replicates of eight main plots (Figure 3.1). Each main plot was split into three split-plots containing the three forms of fertiliser applied. The split-plot treatments were randomised within each main plot.

In 1987 and 1988, applications of 120 kg N/ha were compared under several different split-timing regimes to determine whether split applications would increase nitrogen uptake and yields, without excessively raising the grain nitrogen content. Results from 1987 and 1988 showed that split applications of 120 kg N/ha tended to raise the nitrogen content of the grain above 1.7%.

Table 3.1: Details of sites for study of N requirements for spring-sown malting barley.

	1987		1988		1989	
LOCATION	Bush Lothian (Seafield)	Lintlaw Borders	Bush Lothian (Lower Fulford)	Middlestot Borders	Bush Lothian (March Park)	Upper Cairnie Perthshire
GRID REF.	NT 253 649	NT 839 570	NT 243 648	NT 822 504	NT 249 659	NO 025 193
ELEVATION (m)	180	76	205	85	195	105
SOIL SERIES	Darvel	Hobkirk	(Alluvium)	Whitsome	Easter Bush	Balrownie
TEXTURE	SCL	SL	SL	SCL	SCL	SCL
coarse sand (%)	26.9	15.5	28.4	18.6	29.8	28.9
fine sand	30.5	53.0	32.4	34.2	28.0	30.2
silt	24.1	21.1	23.0	28.7	27.4	25.9
clay	14.5	10.5	16.2	18.6	14.9	15.0
pH	6.1	6.5	6.5	6.7	6.4	6.7
O.M.(%)	3.8	3.0	3.7	2.3	3.4	1.8
VARIETY	Golf	Corgi	Blenheim	Sherpa	Blenheim	Blenheim
PREVIOUS CROPPING						
1988	--	--	--	--	W. barley	Oil seed rape
1987	--	--	W. barley	S. barley	W. barley	W. barley
1986	W. wheat	W. barley	W. barley	W. barley	W. barley	--
1985	Potatoes	S. barley	W. barley	S. barley	W. barley	--
1984	S. barley	Swedes	W. barley	S. barley	--	--
1983	W. barley	W. wheat	--	--	--	--

Table 3.2: Nitrogen application rates and timings

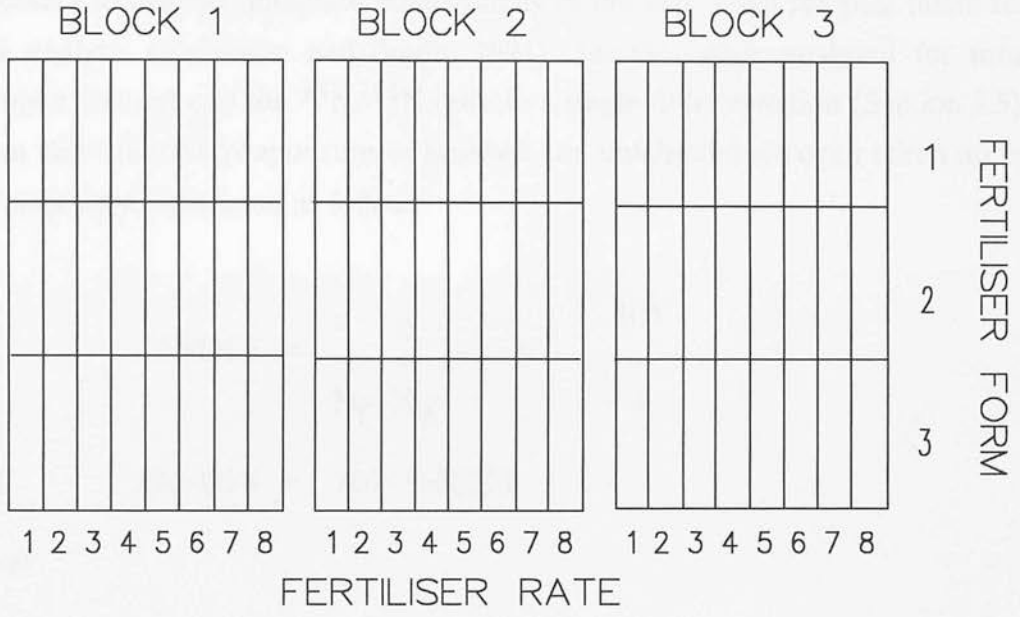
1987, 1988			1989		
Sowing	Brairding (Emergence)	Tillering	Sowing	Brairding (Emergence)	Tillering
0	0	0	0	0	0
60	0	0	60	0	0
90	0	0	90	0	0
120	0	0	120	0	0
150	0	0	45	45	0
60	60	0	45	0	45
60	0	60	0	90	0
0	120	0	60	60	0

Therefore in 1989 it was decided that the fertiliser rate of 90 kg N/ha would also be applied under several split-timing regimes to try to ensure a lower grain nitrogen content.

Labelled ^{15}N fertiliser (ca. 5 atom per cent ^{15}N) was mixed with unlabelled nitrogen fertiliser of the same form (containing ^{15}N at the natural isotopic abundance of 0.366 atom per cent), to dilute the ^{15}N to ca. 0.7 atom per cent, ie about twice the natural abundance. This was done for each of the microplots by dissolving the appropriate weights, corresponding to the required fertiliser rates in 500 ml of water. Small samples of each fertiliser solution were then analysed to confirm the isotopic composition of the fertiliser. Each microplot measured 2 m x 1.5 m, which was sufficient to exclude border effects which could influence the ^{15}N concentrations of plants grown near the edge of the microplot (Sanchez *et al.*, 1987; Follet *et al.*, 1991). Plants grown 0.5 m or further from the edge of the microplot have no border effects (Follet *et al.*, 1991).

To each 2 m x 1.5 m microplot, the solution was applied by a hand-operated sprayer (Plate 3.1). The spray was applied in a steady pattern of cross-sweeps to ensure a uniform application of fertiliser. The remainder of each split plot received the equivalent rate of hand-broadcast unlabelled fertiliser at the

Figure 3.1: Experimental Plot Design 1987-1989.



same rate. Plastic covers were placed over the ^{15}N microplots while the unlabelled fertiliser was applied to ensure that there was no contamination with this ^{15}N fertiliser (Plate 3.2). On each subsequent occasion when more nitrogen fertiliser was applied, a separate microplot was treated with labelled nitrogen while the remaining area (including the microplot previously receiving labelled nitrogen) received unlabelled fertiliser.

3.1.2: Plant sampling, preparation and analysis

Plant samples were taken from the microplots on up to five occasions during the growing season. Two 0.5 m rows were cut on each occasion to within a few mm of ground level. Simultaneously, larger areas (0.5 m^2) were sampled from the unlabelled parts of the plots for dry matter determination. All plant

samples were oven dried at 100 ^{o}C. Dry matter yields were recorded and then the dry matter samples discarded. Samples from the ^{15}N-treated microplots were milled in a hammer mill and then sub-samples (5 g) were finely ground in an agate ball mill to produce a very fine flour-like consistency. This was necessary to achieve adequate homogeneity in the very small samples taken for ^{15}N analysis (Robinson and Smith, 1991). Samples were analysed for total nitrogen content and the $^{15}N/^{14}N$ ratio in a single determination (Section 3.5). From this ratio the proportions of labelled and unlabelled nitrogen taken up by the crop were calculated as follows:

$$\%NDFF = \frac{x - N_0}{N_f - N_0} \times \frac{100}{1}$$

and $$\%NDFS = 100 - \%NDFF$$

where

%NDFF = % nitrogen derived from fertiliser
%NDFS = % nitrogen derived from soil
x = ^{15}N abundance of sample
N_0 = Natural background ^{15}N abundance
N_f = ^{15}N abundance of fertiliser applied

The N uptake was then calculated as follows:

Total N uptake = %N x Plant dry weight
Labelled N uptake = Total N uptake x %NDFF
Unlabelled N uptake = Total N uptake - Labelled N uptake

Fertiliser N uptake was also calculated without the need for ^{15}N data as follows:

Fertiliser N uptake = Total N uptake in the fertilised plots
- Total N uptake in the unfertilised plots

Plate 3.2: Application of ^{14}N-labelled fertiliser to the rest of the plot ensuring that there is no contamination of the ^{15}N-labelled microplot.

Plate 3.1: Application of ^{15}N-labelled fertiliser solution to the soil surface of 2m x 1.5 m microplot.

3.1.3: Sampling dates

Details of sampling dates and growth stages of the trial plots at the sites between 1987 and 1989 are as follows.

1987	*Lintlaw*	
Sown	26/3/87	
Cut 1	20/5/87	3 tillers
Cut 2	3/6/87	4-5 tillers
Cut 3	17/6/87	
Cut 4	1/7/87	Ear half emerged (GS 55)[a]
Cut 5	15/7/87	
Harvest	31/8/87	

(a): Zadoks *et al.* (1974).

1987	*Bush (Seafield)*	
Sown	16/4/87	
Cut 1	20/5/87	3 tillers
Cut 2	2/6/87	3-4 tillers
Cut 3	16/6/87	
Cut 4	30/6/87	Booting (GS 49)
Cut 5	14/7/87	
Harvest	9/9/87	

1988	*Middlestot*	
Sown	11/3/88	
Cut 1	16/5/88	5 leaves on main stem, 2-3 tillers
Cut 2	6/6/88	Stem elongation; 3 nodes
Cut 3	27/6/88	Ear emergence
Cut 4	17/7/88	Grain medium milk (GS 75)
Cut 5	8/8/88	Caryopsis hard (GS 90)
Harvest	15/8/88	

1988 *Bush (Lower Fulford)*

Sown	5/4/88	
Cut 1	26/5/88	5 leaves on main stem, 3 tillers
Cut 2	16/6/88	Stem elongation; 3 nodes
Cut 3	6/7/88	Ear emergence
Cut 4	28/7/88	Grain medium milk (GS 75)
Cut 5	18/8/88	Grain hard dough (GS 89)
Harvest	30/8/88	

1989 *Upper Cairnie*

Sown	4/4/89	
Cut 1	24/5/89	4 leaves on main stem, 1-2 tillers
Cut 2	15/6/89	Stem elongation; 4 nodes; 3 tillers
Cut 3	4/7/89	Ear emergence
Cut 4	25/7/89	Grain medium dough (GS 85)
Harvest	21/8/89	

1989 *Bush (March Park)*

Sown	31/3/89	
Cut 1	17/5/89	5 leaves on main stem, 2-3 tillers
Cut 2	7/6/89	Stem elongation; 2 nodes
Cut 3	27/6/89	Anthesis
Cut 4	18/7/89	Grain early dough (GS 83)
Cut 5	1/8/89	Caryopsis hard (GS 92)
Harvest	15/8/89	

3.1.4: Soil sampling and analysis

3.1.4.1: Soil sampling and routine analysis

Soil samples were taken at intervals during the growing season. Samples from an area of approximately 0.15 m^2 were dug with a spade to depths of 0-20 cm and 20-40 cm, then mixed and subsampled in the field. The subsamples were stored frozen (-15 ^oC) until analysis could be carried out. Measurements of soil texture, pH and organic matter were made on the complete 0-40 cm horizon. Soil texture was determined by particle size analysis (Gee and Bauder, 1986). Soil pH was determined in water (McLean, 1982). Soil organic matter was determined by the Walkley-Black method (Allison, 1965). Results are presented in Tables 3.1 and 3.3.

3.1.4.2: Available nitrogen analysis

Available nitrogen analysis was carried out on the 0-20 cm and 20-40 cm horizons. Soil samples were sieved to remove stones and plant debris. 20 g samples of fresh soil were weighed into 250 ml conical flasks and shaken with 100 ml of 1M KCl extracting solution for one hour. The extracting solution was then filtered (Whatman No.42 filter paper) and ammonium- and nitrate-N determined by continuous flow analysis using the methods of Crooke and Simpson (1971), and Henrikson and Selmer-Olsen (1970), respectively. In 1990 these separate analysis systems were replaced with a Chemlab Instruments Ltd. system. Ammonium-N was still determined by the same procedure (Crooke and Simpson, 1971), but the nitrate-N procedure now used copper and hydrazine in place of cadmium as a reducing agent.

3.1.4.3: Potentially available soil nitrogen

Potentially mineralisable nitrogen was determined on the 0-20 cm soil horizon by two hydrolysis techniques: these were slightly modified versions of those devised by Whitehead (1981), and by Gianello and Bremner (1986a). In the modified Whitehead method 12 g of fresh soil were boiled with 80 ml of 1M KCl for one hour in a 500 ml reflux flask. After cooling, the suspension was

filtered (Whatman No.42) and the extract analysed for ammonium-N, (Section 3.1.4.2). A separate sample of the same soil was analysed at the same time to measure the amount of ammonium-N present at the start. The amount of potentially mineralisable nitrogen present in any soil was the difference between these two measured values. In the Gianello and Bremner method 12 g of fresh soil were refluxed with 80 ml 2M KCl for four hours. Subsequent analysis was the same as for the Whitehead method.

3.2: 1990 Season

3.2.1: Site preparation and fertiliser application

In 1990 the effect of different sites on the uptake of soil nitrogen was examined more closely. Trials were set up at six sites (Table 3.3) with a reduced number of fertiliser rates and forms. Two sites, one on the Edinburgh School of Agriculture's Bush Estate (Crofts) and Treaton, were located within larger trial sites managed by CPAD and the procedure followed was the same as in the previous three years (Section 3.1.1). Three of the other sites were situated on commercial farms and the fourth was situated elsewhere on the Bush Estate.

At the four sites not managed by CPAD, the trial plot area was left unfertilised after sowing while the rest of the field was fertilised with NPK compound fertiliser by the farm staff. P and K fertiliser was hand-broadcast over the plot area at the same rate as the rest of the field. Then a single rate (120 kg N/ha) of nitrogen fertiliser was applied in only two fertiliser forms, ammonium sulphate and ammonium nitrate, together with a zero N control treatment. The trials were laid out in a randomised block design with three replicates of two plots, with each fertiliser form as one of two splitplots within each main plot. The ^{15}N-labelled and unlabelled fertilisers were applied to the appropriate areas as described above (Section 3.1.1). Sampling procedures were also carried out as above, except that larger samples from 1 m^2 were taken for dry matter determination, and there were only four sampling dates during the growing season.

Table 3.3: Details of 1990 sites for study of N requirements for spring-sown malting barley.

LOCATION	Manorhill Borders	Quixwood Borders	Bush Lothian (Crofts)	Bush Lothian (F. Holding)	Treaton Fife	Kettle Fife
GRID REF.	NT 659 318	NT 785 632	NT 246 251	NT 253 657	NO 324 024	NO 293 078
ELEVATION (m)	105	195	190	175	90	45
SOIL SERIES	Smailholm	Ettrick	(Alluvium)	E. Bush/ Macmerry	Darvel	Eckford
TEXTURE	SL	CL	SL	SCL	SL	LS
coarse sand (%)	26.2	16.8	30.7	29.0	34.4	32.2
fine sand	34.4	19.4	25.8	26.6	32.3	48.6
silt	26.9	42.2	25.6	28.8	20.5	11.4
clay	12.5	21.6	18.0	15.6	12.8	6.7
pH	6.1	6.2	5.7	6.0	6.4	6.7
O.M.(%)	2.4	5.1	4.7	3.3	5.7	2.8
VARIETY	Camargue	Blenheim	Blenheim	Blenheim	Blenheim	Blenheim
PREVIOUS CROPPING						
1989	W. barley	S. barley	W. wheat	W. wheat	S. barley	Br. sprout
1988	W. wheat	W. barley	Potatoes	Potatoes	S. barley	W. barley
1987	Potatoes	S. barley	S. barley	W. barley	W. wheat	W. barley
1986	S. barley	W. wheat	W. barley	S. barley	Potatoes	Calabrese

3.2.2: Sampling dates

Details of the sampling dates for each of the trial sites in 1990 and the crop growth stage at the time of each sampling are as follows.

Manorhill

Sown	25/3/90	
Cut 1	14/5/90	4-5 leaves on main stem, 4 tillers
Cut 2	8/6/90	Stem elongation; 3 nodes
Cut 3	10/7/90	Caryopsis water ripe (GS 72)
Harvest	8/8/90	

Quixwood

Sown	31/3/90	
Cut 1	14/5/90	4 leaves on main stem, 3 tillers
Cut 2	12/6/90	Stem elongation; 3 nodes
Cut 3	12/7/90	Grain early milk stage (GS 74)
Harvest	29/8/90	

Bush (Crofts)

Sown	30/3/90	
Cut 1	23/5/90	6 leaves on main stem; 3-5 tillers
Cut 2	20/6/90	Booting (GS 49)
Cut 3	16/7/90	Grain medium milk (GS 75)
Harvest	27/8/90	

Bush (Farmer's Holding)

Sown	2/4/90	
Cut 1	23/5/90	5 leaves on main stem, 3-4 tillers
Cut 2	21/6/90	Start of ear emergence (GS 53)
Cut 3	16/7/90	Grain medium milk (GS 76)
Harvest	20/8/90	

Treaton

Sown	28/3/90	
Cut 1	17/5/90	5 leaves on main stem, 1-3 tillers
Cut 2	19/6/90	Start of ear emergence (GS 53)
Cut 3	17/7/90	Grain medium milk (GS 76)
Harvest	22/8/90	

Kettle

Sown	25/4/90	
Cut 1	4/6/90	6 leaves on main stem, 4-5 tillers
Cut 2	25/6/90	Booting (GS 49)
Cut 3	19/7/90	Grain early milk (GS 74)
Harvest	31/8/90	

3.3: Monthly Rainfall at Trial Sites

Rainfall data was recorded at the Bush Estate in each of the four years that trials were carried out, and 'on site' at the Middlestot, Upper Cairnie and Treaton sites between 1988 and 1990. Data given for Lintlaw in 1987, and Manorhill, Quixwood and Kettle in 1990, were obtained from measuring stations at locations close to the appropriate site (Table 2.4).

Table 2.4: Monthly rainfall data (mm) at barley trial sites.

		March	April	May	June	July	August	September
1987	Lintlaw	79	69	37	72	77	100	35
1987	Bush	84	67	57	98	86	101	65
1988	Middlestot	--	42(a)	66	36	161	50(b)	--
1988	Bush	76	65	60	20	143	76	--
1989	U. Cairnie	80	39	25	37	24	43(b)	--
1989	Bush	87	35	38	69	15	114	--
1990	Manorhill	25	22	42	58	55	46	--
1990	Quixwood	14	19	28	114	39	44	--
1990	Bush	57	27	39	110	55	68	--
1990	Treaton(c)	22	30	22	123	29	44	--
1990	Kettle(c)	22	30	22	123	29	44	--

(a): recording started on 10/4/88
(b): recording completed at harvest: Middlestot 22/8/88, U. Cairnie 20/8/89
(c): data from 12/6/90 collected from weather station at Treaton; data prior to this lost due to recorder malfunction and replaced with data from Met. Office weather station 884437

3.4: Mineralisation/Immobilisation Turnover in the Field

In 1989 and 1990 experiments were set up to determine the gross mineralisation, immobilisation and nitrification of nitrogen in the soil under the barley crops grown at the various sites. The experiments involved the use of single-labelled ^{15}N ammonium nitrate in paired microplots using a method described by Barraclough (1988), and Barraclough and Smith (1987) (Section 2.5)

3.4.1: 1989 season

3.4.1.1: Experimental design and fertiliser application

In 1989, experiments were set up at both trial sites covering three separate periods during the growing season. The actual dates covered by each experimental period at each site were as follows.

	Period 1	Period 2	Period 3
Bush	13/4/89-4/5/89	31/5/89-22/6/89	13/7/89-3/8/89
U.Cairnie	14/4/89-5/5/89	30/5/89-20/6/89	12/7/89-2/8/89

These periods covered germination/seedling growth, stem elongation and grain filling, respectively. Two treatments were compared in each period at Upper Cairnie, and in the first two periods at the Bush site. At Bush there was only enough space for one treatment to be studied in the third period. The treatments compared looked at the effect of nitrogen form on the rates of mineralisation/immobilisation in the soil. However, as the technique requires the application of both NH_4-N and NO_3-N, this meant that the treatments could only vary in the ratio of [NH_4] to [NO_3]. Treatment 1 contained high NH_4-N (70% NH_4:30% NO_3), and Treatment 2 contained low NH_4-N (30%

NH_4:70% NO_3). At Bush the treatment applied for Period 3 was 50% NH_4:50% NO_3.

Three replicate plots were laid out for each treatment and each time period in a randomized block design within the main experimental area. Adjacent duplicate microplots, 1 m x 1 m, were sprayed with the appropriate nitrogen fertiliser solution, one microplot receiving $^{15}NH_4$ and the other receiving $^{15}NO_3$. Each microplot received 5 litres of water to wash the solution into the soil. The first nitrogen fertiliser application, immediately after sowing, was at a rate of 120 kg N/ha and 3 atom % ^{15}N. The surrounding area received unlabelled nitrogen fertiliser at the same rate, and in the same form. For the second and third time periods, microplots were marked out in the areas which had received unlabelled nitrogen fertiliser at sowing. On these occasions the ^{15}N was applied at a very low nitrogen rate, to minimise the effect of late additions of fertiliser nitrogen. A solution containing 10 kg N/ha at 10 atom % ^{15}N was sprayed onto these microplots, which had received 120 kg N/ha of unlabelled nitrogen fertiliser at sowing. The higher enrichment of ^{15}N was necessary to allow detection of this ^{15}N in the plant and soil samples from such a small input of fertiliser nitrogen.

3.4.1.2: Sampling and analysis

Plant samples were taken at the beginning and the end of each time period. Cuts comprising 2 rows x 0.5 m were taken from the microplots for ^{15}N analysis and 0.5 m^2 cuts were taken for dry matter analysis. Soil samples (0-30 cm) were also taken from the microplots for mineral N and ^{15}N analysis.

To ensure sufficient nitrogen was present for an accurate analysis of ^{15}N content, 200 g of fresh soil were shaken with 1 litre of 1M KCl for one hour. The filtered extract was evaporated to approximately 300 ml. Ammonium-N was released as NH_3 by the addition of 10 g of magnesium oxide and then the solution was steam-distilled for 6 minutes. The distillate was collected in a flask containing 10 ml of 2% boric acid/indicator solution. This was made slightly

acid (to prevent ammonia volatilisation) by the addition of a few ml of 0.01M sulphuric acid which was indicated by a colour change from green to red (Hauck, 1982). The solution was then evaporated to dryness, in which state it was ready for ^{15}N analysis. The original filtered extract (minus the ammonium-N which had been distilled out) was transferred to a second steam-distillation unit, and with the addition of 15 g Devarda's Alloy was distilled for a further six minutes to reduce the nitrate-N to ammonia. Again the distillate was collected in a flask containing 10 ml of 2% boric acid/indicator solution, acidified and evaporated. Between samples the distillation units were cleaned by distilling 20 ml of ethanol through the system for three minutes (Hauck, 1982).

3.4.2: 1990 season

In 1990, measurements were extended to the six sites of the main experiment. In this season, there was less space available and the experiment was limited to only one time period and one rate of nitrogen applied, i.e. 60:60 NH_4:NO_3. ^{15}N fertiliser solution was applied at the start of the experiment as described above (Section 3.4.1.1). The periods covered by the experiments at each site are given below.

Site	Period
Manorhill	16/5/90 - 6/6/90
Quixwood	16/5/90 - 6/6/90
Bush (Crofts)	25/5/90 - 15/6/90
Bush (F.Holding)	25/5/90 - 15/6/90
Treaton	17/5/90 - 7/6/90
Kettle	4/6/90 - 25/6/90

Unlabelled fertiliser NH_4NO_3 was applied at sowing at a rate of 120 kg N/ha, and 10 kg N/ha as NH_4NO_3 solution was sprayed onto duplicate microplots, either as $^{15}NH_4NO_3$ or as $NH_4{}^{15}NO_3$ at the beginning of the experimental period on the first date listed above for each site.

3.5: Mass Spectrometery

3.5.1: General principles

The technique of mass spectrometery determines the isotopic composition of a sample by separating out charged ions on the basis of their mass to charge (m/e) ratio and determining their relative proportions (Robinson and Smith, 1991). In the case of nitrogen analysis this involves the conversion of the N in the sample to N_2. These N_2 molecules are then ionised and passed through a magnetic field which separates the N into three components: $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ with masses of 28, 29 and 30 respectively. The relative amounts of each component are measured and from this the ^{15}N content of the sample can be calculated.

$$\text{Atom \% } ^{15}N = (\text{No. } ^{15}N \text{ atoms / total No. N atoms}) \times 100$$

This can be calculated using the values obtained for $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ values as follows:-

$$\text{Atom \% } ^{15}N = [(^{30}N + 1/2 \times ^{29}N) / (^{28}N + ^{29}N + ^{30}N)] \times 100$$

For detailed reviews on aspects of mass spectrometery see Hauck (1982) and Robinson and Smith (1991).

3.5.2: Experimental procedure

Plant and soil extract samples were analysed for ^{15}N content using a VG Isogas MM622 mass spectrometer linked to a Carlo-Erba 1400 automatic N analyser, which converts nitrogen compounds to N_2 by the Dumas oxidation-reduction procedure. Subsamples of the prepared plant material (Section 3.1.2) and the crystallised soil extracts (Section 3.4.1.2) were accurately weighed out into small tin cups and sealed for analysis. In this system at least 100 μg of N is required to give an accurate reading. For young plant samples with N contents of 1-1.5 %N or greater, a sample of 10 mg is sufficient. More mature plant

samples (especially straw) and the soil extracts normally require subsamples of 20-30 mg to ensure that there is sufficient N present for analysis.

In the Dumas system (Figure 3.2) the sample is combusted at a very high temperature in a stream of O_2 in an oxidation column packed with NiO. The N in the sample is converted to nitrogen oxides and then to N_2 by reduction by metallic copper. The tin cup acts as a catalyst raising the temperature to ca. 1700 ^{o}C to ensure complete combustion. The helium acts as an inert carrier gas to move the N_2 and other combustion products through the system. H_2O, CO_2 and other contaminants are removed as the N_2 is passed over absorbent columns. Then the N_2 is ionised, and after passing through a magnetic field the ratios of $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ are measured. Reference values are obtained from standards of known N and ^{15}N content which are analysed in the same batch. These standards allow the mass spectrometer computer software to calibrate the ion beam currents and current ratios of the samples and calculate values for total N and ^{15}N.

3.5.3: Checks on variation between samples

The procedure followed during the preparation of samples for analysis in the mass spectrometer required that small sub-samples (10-30 mg) were selected for analysis, upon the assumption that the sample would be homogeneous. Checks carried out have shown that the variability between replicate 5 g subsamples of plant material selected for grinding in the agate ball mill, and that between replicate 10 mg portions of the subsequently ground material were very much less than is commonly observed between replicate field plots (Table 3.4).

As a further check on the accuracy of the data, any samples whose replicate ^{15}N atom % values differed by greater than 0.001 atom % were repeated.

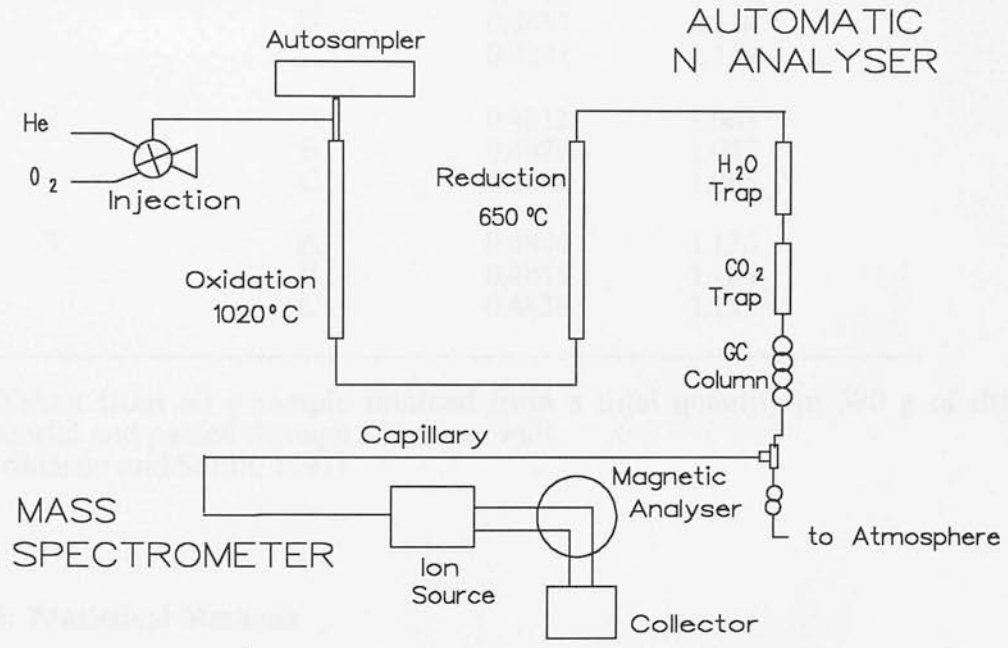


Figure 3.2: Schematic Diagram of Automatic Nitrogen Analyser with Direct Combustion System, Interfaced with Isotope Mass Spectrometer (Robinson and Smith, 1991).

Table 3.4: Variation in ^{15}N and Total N Content of Dried, Ground Plant Material (Barley) as Determined by a Direct Combustion Method

Subsample for ball-milling (5 g)[a]	Replicate portion of subsample after ball-milling (ca. 10 mg)	^{15}N (atom %)	Total N (% dry wt.)
1	A	0.4822	1.135
	B	0.4833	1.114
	C	0.4831	1.119
2	A	0.4813	1.083
	B	0.4820	1.057
	C	0.4818	1.065
3	A	0.4844	1.156
	B	0.4845	1.189
	C	0.4839	1.137

[a] Taken from 60 g sample retained from a total quantity of 580 g of dried material and passed through a hammer mill.
(Robinson and Smith, 1991)

3.6: Statistical Methods

The analysis of variance was carried out using the Genstat IV package (Lawes Agricultural Trust, Harpenden). Data were stored and prepared for Genstat analysis using Minitab (Release 7.1). A split-plot analysis of variance was performed on each of the main variables measured, on each sampling occasion at each site. Significant differences in the main treatment of nitrogen rate/timing are discussed. Also discussed are significant differences between fertiliser forms. The standard errors of the differences between means (SED) shown, calculated by Genstat, were the SED between the means of any two treatments. The degrees of freedom (df) given for each SED were the degrees of freedom associated with the residual error for that analysis of variance. The SED values calculated by Genstat did not take into account the effect of missing values. Where appropriate SED values were adjusted using the procedure set out by Cochran and Cox (1957). In 1990 the statistical analyses were similar,

except that the analyses of variance were expanded to include the variation between the six sites studied.

Results showing variation over the growing season were analysed for each site using an analysis of variance which covered all the sampling dates and treatments in that season. The SED values given for these results show the SED between the means of any fertiliser form at any sampling date, for the nitrogen rate/timing treatment shown.

4: NITROGEN UPTAKE AND GRAIN NITROGEN CONTENT

4.1: Grain Nitrogen Content and Yield, 1987-1989

Concentrations of nitrogen in the grain at each site 1987-1989, over a range of fertiliser nitrogen treatments are shown in Figures 4.1-4.3. The grain yields for the equivalent treatments are shown in Tables 4.1-4.6.

4.1.1: 1987

In 1987 the percentage nitrogen content in the grain increased with increasing rates of fertiliser nitrogen applied at both sites (Figure 4.1). There was little effect of fertiliser form except at 150 kg N/ha fertiliser nitrogen applied when the calcium nitrate treatment was significantly higher than the other fertiliser nitrogen forms giving a grain nitrogen content of 1.81 % at Lintlaw. At Lintlaw split or late fertiliser nitrogen applications at the 120 kg N/ha level increased grain nitrogen contents in all treatments when applied in the form of calcium nitrate, but only the seedbed-tillering split-application treatment increased grain nitrogen concentrations for the ammonium fertiliser forms. Results presented for Bush are restricted to treatments where the fertiliser nitrogen was only applied at sowing. A mistake, when applying the later applications of unlabelled fertiliser, resulted in the contamination of split-treatment microplots which should have received only labelled nitrogen. Therefore the results presented are restricted to data calculated from the uncontaminated microplots.

At Lintlaw grain yields in response to fertiliser all applied at sowing levelled off at 90 kg N/ha and above, at approximately 7.5 t/ha, except for applications in the form of ammonium sulphate which resulted in a linear increase up to 8.3 t/ha when 150 kg N/ha was applied (Table 4.1). At the 120 kg N/ha level, there was a significant increase in yield of around 1 t/ha following applications split between sowing and tillering. Calcium nitrate applications also resulted in an increased yield when split between sowing and emergence, rising from 7.5 t/ha up to 8.9 t/ha.

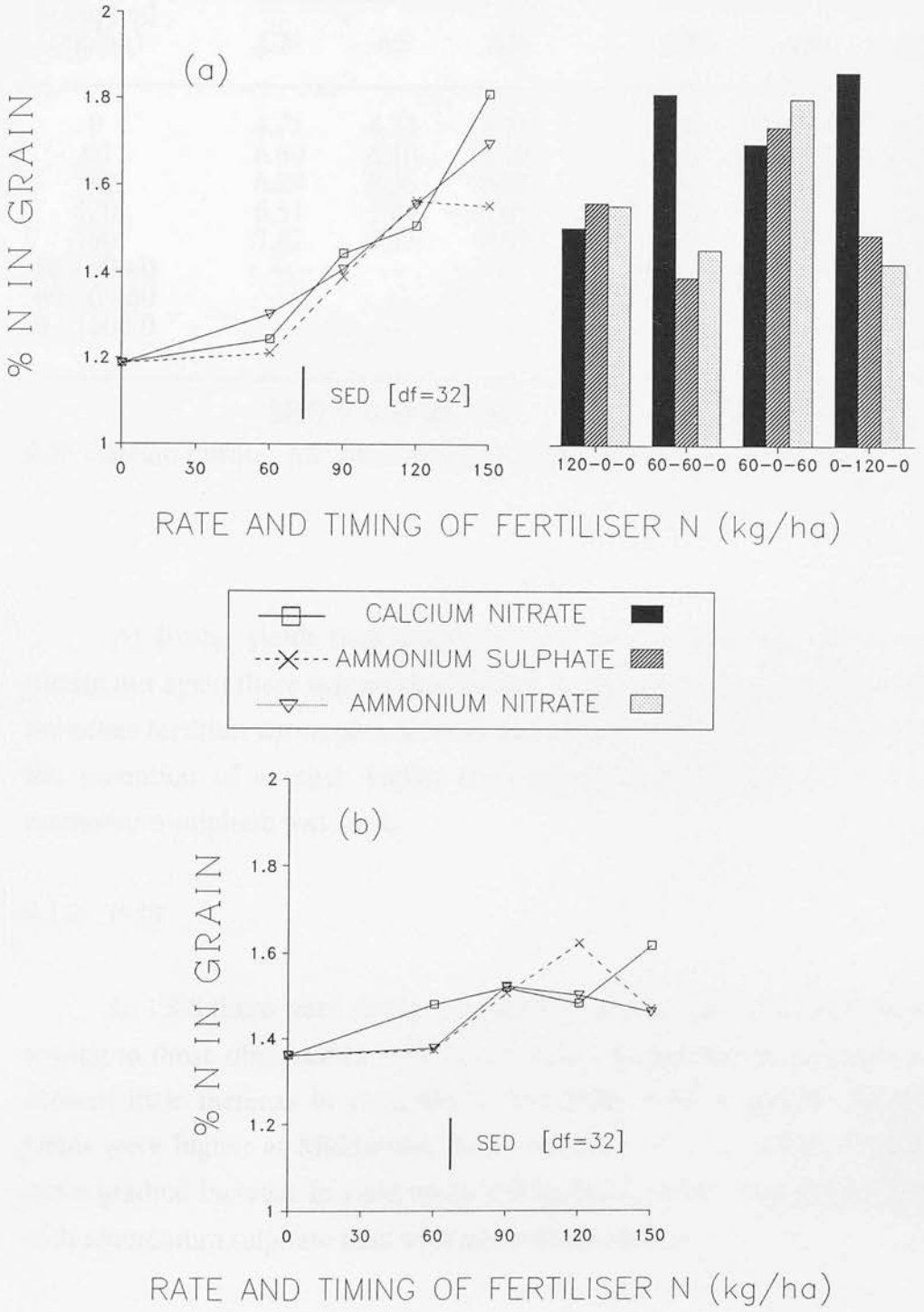


Figure 4.1. Nitrogen content in the grain (%) in spring barley as influenced by the rate and timing of fertiliser nitrogen applications, harvest 1987, (a) Lintlaw, (b) Bush (Seafield)

Table 4.1: Grain yields (t/ha, 15 % moisture) as affected by fertiliser nitrogen applications at two sites, 1987.

N applied (kg/ha)	Bush (Seafield)			Lintlaw		
	CN	AS	AN	CN	AS	AN
0	4.71	4.71	4.71	3.74	3.74	3.74
60	6.60	6.10	5.10	6.01	4.86	6.29
90	6.89	8.36	6.94	7.47	6.72	7.35
120	6.51	7.04	7.67	7.48	7.28	7.21
150	7.67	7.81	8.97	6.33	8.28	7.72
60+60+0	--	--	--	8.91	6.69	7.13
60+0+60	--	--	--	8.45	8.25	8.16
0+120+0	--	--	--	6.36	7.30	7.68
	SED = 0.94 [df=20]			SED = 1.09 [df=32]		

CN: calcium nitrate; AS: ammonium sulphate; AN: ammonium nitrate

At Bush, yields rose steeply in response to the lower rate of calcium nitrate but again there was no significant rise above 90 kg N/ha applied. Both of the other fertiliser forms gave a linear increase in yield up to 150 kg N/ha, with the exception of a much higher than expected yield at 90 kg N/ha when ammonium sulphate was used.

4.1.2: 1988

In 1988 there were similar responses of grain yield to nitrogen applied at sowing to those observed in 1987 (Table 4.2). Calcium nitrate treatments again showed little increase in yield above 90-120 kg N/ha at either site although yields were higher at Middlestot. Both the other fertiliser forms resulted in a more gradual increase in yield up to 150 kg N/ha; yields were generally higher with ammonium sulphate than with ammonium nitrate.

Table 4.2: Grain yields (t/ha, 15 % moisture) as affected by fertiliser nitrogen applications at two sites, 1988.

N applied (kg/ha)	Bush (Lower Fulford)			Middlestot		
	CN	AS	AN	CN	AS	AN
0	3.21	3.21	3.21	2.23	2.23	2.23
60	4.08	4.33	4.12	7.11	3.71	4.30
90	5.38	5.68	5.20	6.40	5.40	5.33
120	5.11	5.98	5.44	7.10	5.98	5.52
150	4.86	7.18	5.52	7.28	6.98	6.30
60+60+0	5.22	5.66	6.01	6.50	6.35	6.34
60+0+60	4.88	6.07	5.28	5.91	6.13	5.91
0+120+0	6.11	6.18	5.50	6.44	6.32	7.13
	SED = 0.73 [df=32]			SED = 0.76 [df=32]		

CN: calcium nitrate; AS: ammonium sulphate; AN: ammonium nitrate

Grain nitrogen contents (Figure 4.2) were affected little by fertiliser form; mean contents following ammonium nitrate applications were lowest at all rates at Middlestot, but the differences were not significant (Figure 4.2b).

Overall, grain from Middlestot had much lower nitrogen contents than that from Bush, being under 1.6 % N at all nitrogen rates up to 150 kg N/ha. There was little effect of the timing of fertiliser application at either site. The lower grain nitrogen concentrations appeared to be caused by several factors. Generally grain yields were higher at Middlestot, which meant that there was a greater dilution of nitrogen in the grain by photosynthate during the grain-filling period. This was compounded by the fact that total nitrogen uptake was lower than at Bush in 1987, mainly due to a reduced uptake of unlabelled nitrogen.

Easson (1984) reported that there was little increase in the grain nitrogen contents of spring barley grown in Northern Ireland with split applications of fertiliser nitrogen up to tillering. It was reported that grain yields

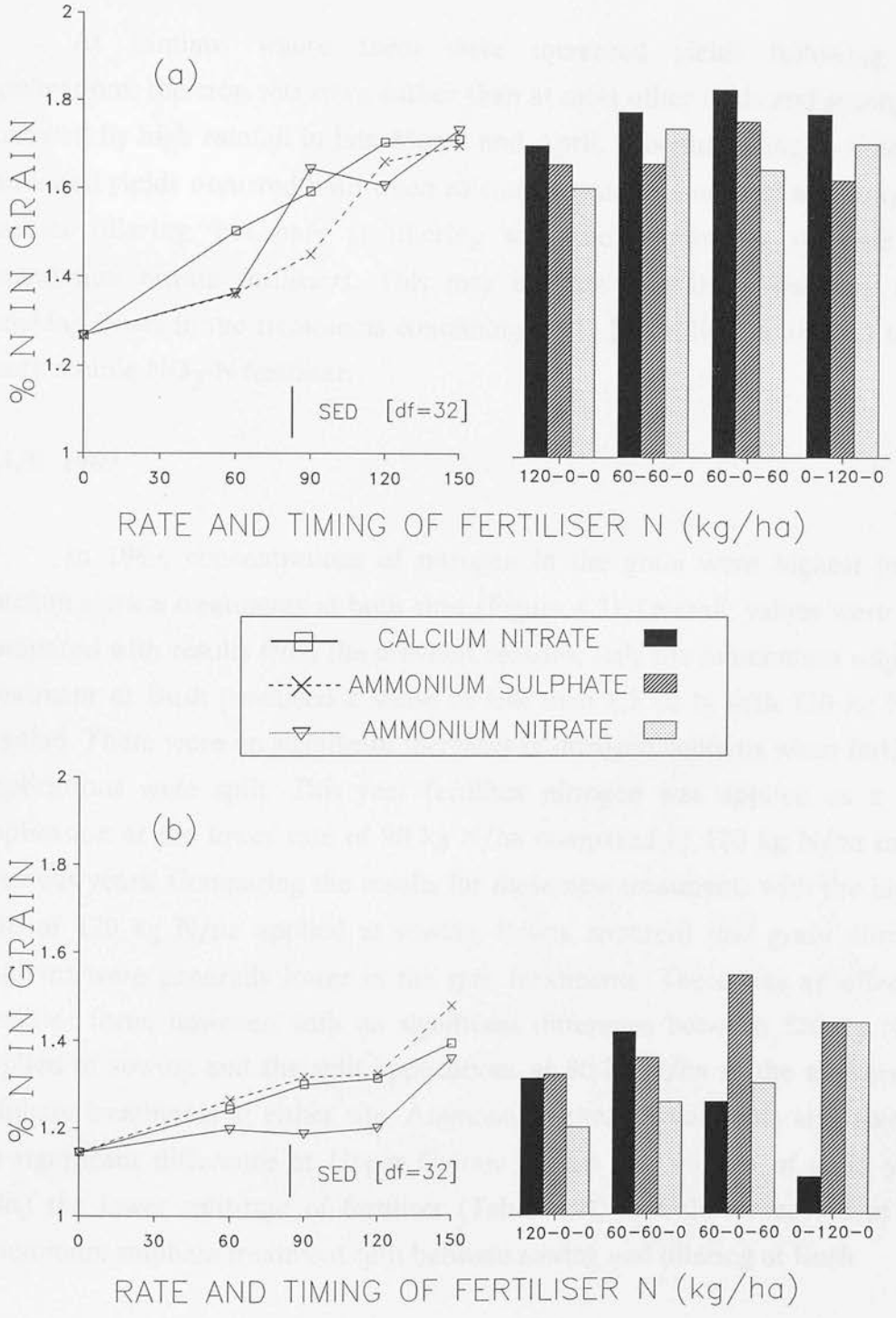


Figure 4.2. Nitrogen content in the grain (%) in spring barley as influenced by the rate and timing of fertiliser nitrogen applications, harvest 1988, (a) Bush (Lower Fulford), (b) Middlestot

were increased by split applications of nitrogen only on an earlier sown crop where there had been considerable rainfall after sowing. This led to greater leaching losses of seed-bed applied nitrogen before the crop had developed sufficiently to compete for nitrogen uptake.

At Lintlaw, where there were increased yields following split applications, the crop was sown earlier than at most other trials and sowing was followed by high rainfall in late March and April. It is interesting to note that increased yields occurred both when calcium nitrate was applied at emergence and at tillering, but only at tillering with the ammonium sulphate and ammonium nitrate fertilisers. This may indicate that there was less rapid leaching losses in the treatments containing NH_4-N fertiliser compared to the more mobile NO_3-N fertiliser.

4.1.3: 1989

In 1989, concentrations of nitrogen in the grain were highest in the calcium nitrate treatments at both sites (Figure 4.3). Overall, values were high compared with results from the previous seasons; only the ammonium sulphate treatment at Bush produced a value of less than 1.7 % N with 120 kg N/ha applied. There were no significant increases in nitrogen contents when fertiliser applications were split. This year fertiliser nitrogen was applied as a split application at the lower rate of 90 kg N/ha compared to 120 kg N/ha in the previous years. Comparing the results for these new treatments with the higher rate of 120 kg N/ha applied at sowing, it was apparent that grain nitrogen contents were generally lower in the split treatments. There was an effect of fertiliser form, however, with no significant difference between 120 kg N/ha applied at sowing and the split applications at 90 kg N/ha in the ammonium sulphate treatments at either site. Ammonium nitrate treatments also showed no significant difference at Upper Cairnie. There was no loss of grain yield using the lower split-rate of fertiliser (Table 4.3), with the exception of the ammonium sulphate treatment split between sowing and tillering at Bush.

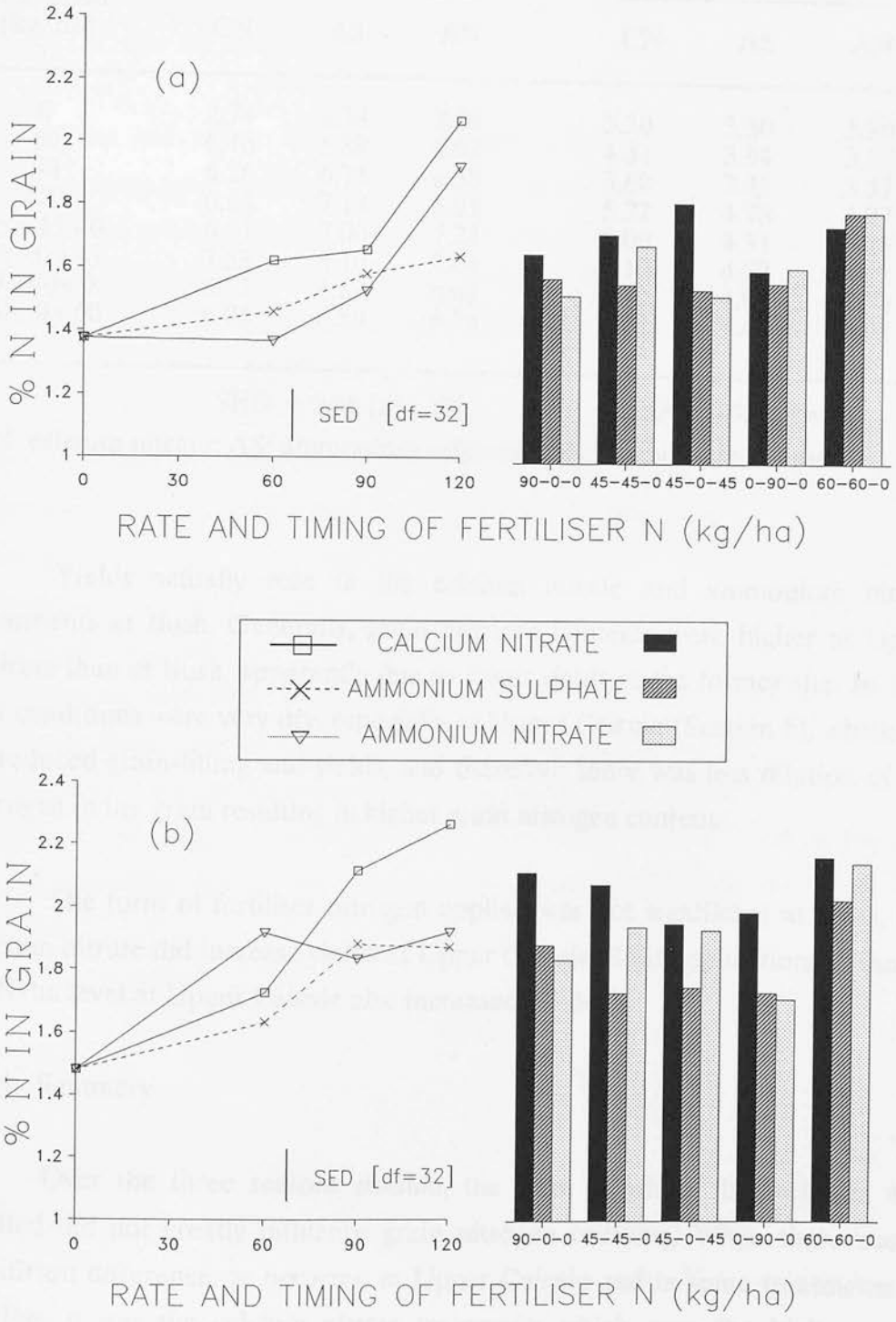


Figure 4.3. Nitrogen content in the grain (%) in spring barley as influenced by the rate and timing of fertiliser nitrogen applications, harvest 1989, (a) Bush (March Park), (b) Upper Cairnie

Table 4.3: Grain yields (t/ha, 15 % moisture) as affected by fertiliser nitrogen applications at two sites, 1989.

N applied (kg/ha)	Bush (March Park)			Upper Cairnie		
	CN	AS	AN	CN	AS	AN
0	2.74	2.74	2.74	3.30	3.30	3.30
60	6.46	5.88	6.67	4.31	3.94	3.52
90	6.26	6.71	6.38	3.68	3.41	3.87
120	6.65	7.18	5.91	5.22	4.78	4.27
45+45+0	6.71	7.00	7.24	5.00	4.31	4.25
45+0+45	7.53	6.10	7.09	5.10	4.57	4.12
0+90+0	6.72	6.62	6.63	4.70	4.96	3.76
60+0+60	6.03	6.59	6.36	4.79	4.42	5.08
	SED = 0.66 [df=32]			SED = 0.45 [df=32]		

CN: calcium nitrate; AS: ammonium sulphate; AN: ammonium nitrate

Yields actually rose in the calcium nitrate and ammonium nitrate treatments at Bush. Generally, grain nitrogen contents were higher at Upper Cairnie than at Bush, apparently due to lower yields at the former site. In 1989 soil conditions were very dry, especially at Upper Cairnie (Section 5), which led to reduced grain-filling and yields, and therefore there was less dilution of the nitrogen in the grain resulting in higher grain nitrogen contents.

The form of fertiliser nitrogen applied was not significant at Bush, but calcium nitrate did increase yields at Upper Cairnie. Split applications at the 90 kg N/ha level at Upper Cairnie also increased yields.

4.1.4: Summary

Over the three seasons studied, the form in which the fertiliser was applied did not greatly influence grain nitrogen contents. When there was a significant difference, as occurred at Upper Cairnie and in some treatments at Lintlaw, it was the calcium nitrate treatments which gave the higher grain

nitrogen contents. This was due to a higher nitrogen uptake in these treatments compared to the other fertiliser forms (Section 4.2). Widdowson *et al.* (1964) found with spring barley that lower grain nitrogen contents in ammonium sulphate fertilised treatments were due to a less efficient recovery of fertiliser nitrogen compared to calcium nitrate fertiliser treatments when fertiliser was broadcast onto the soil surface.

Site and season had a much greater effect on grain nitrogen contents than fertiliser form (Figure 4.4). Generally, at each site there was a fairly linear increase in grain nitrogen contents with increasing fertiliser application and, crucially, the relative differences in content of soil-derived nitrogen (zero fertiliser rate) were maintained over most or all of the range of fertiliser rates. The differences in grain nitrogen contents between sites cannot be fully accounted for seasonal effects only, as there were also significant differences in grain nitrogen contents between sites in the same season. It must be concluded that the grain nitrogen content was significantly related to the available soil nitrogen reserves. Batey and Reynish (1976) earlier reached a similar conclusion from work in England. Results presented showing nitrogen uptake in the trials between 1987 and 1989 (Section 4.2) demonstrate that the uptake of soil nitrogen between sites is more variable than the uptake of fertiliser nitrogen. Climatic conditions, however, must also be taken into account and it is clear that the very high grain nitrogen contents reported for Upper Cairnie were not due to a very high soil nitrogen uptake, but rather were a result of low grain yields probably due to the very dry soil conditions limiting the grain filling period.

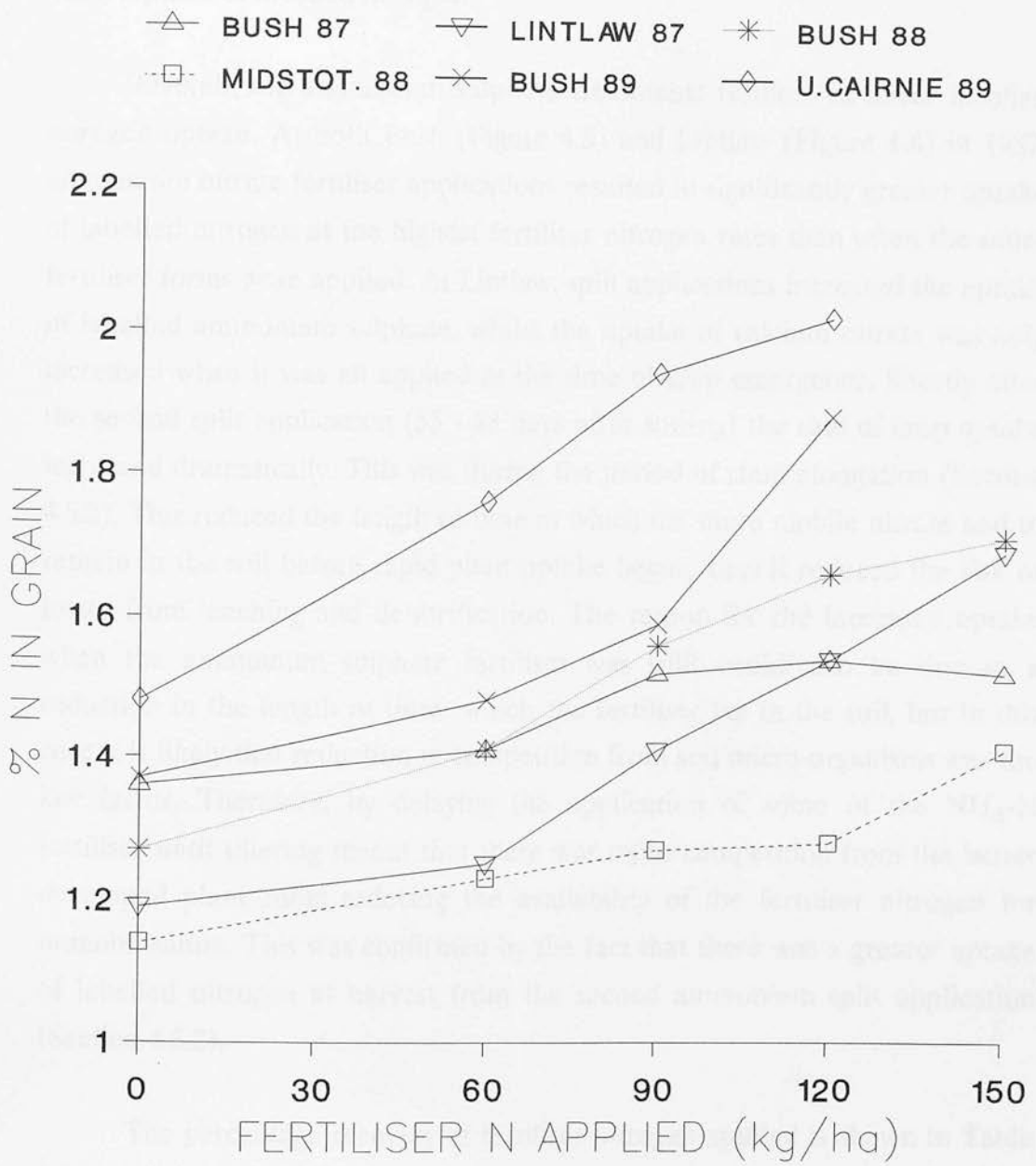


Figure 4.4. Mean nitrogen content in the grain (%) in spring barley as influenced by the rate of fertiliser nitrogen applied at sowing over 6 sites, harvest 1987-1989

4.2: Uptake of Labelled and Unlabelled Nitrogen in Plant Shoots at Harvest, 1987-1989

The uptake of labelled and unlabelled nitrogen is shown for each site in Figures 4.5-4.10. The uptake of labelled nitrogen generally rose linearly with increased fertiliser nitrogen applied, but the uptake of unlabelled nitrogen was generally much more constant over the range of fertiliser applications.

4.2.1: Uptake of labelled nitrogen

Overall, the ammonium sulphate treatments resulted in lower labelled nitrogen uptake. At both Bush (Figure 4.5) and Lintlaw (Figure 4.6) in 1987, ammonium nitrate fertiliser applications resulted in significantly greater uptake of labelled nitrogen at the highest fertiliser nitrogen rates than when the other fertiliser forms were applied. At Lintlaw, split applications increased the uptake of labelled ammonium sulphate, whilst the uptake of calcium nitrate was only increased when it was all applied at the time of crop emergence. Shortly after the second split application (55 - 83 days after sowing) the rate of crop uptake increased dramatically. This was during the period of stem elongation (Section 4.5.2). This reduced the length of time in which the more mobile nitrate had to remain in the soil before rapid plant uptake began, thus it reduced the risk of losses from leaching and denitrification. The reason for the increased uptake when the ammonium sulphate fertiliser was split could also be due to a reduction in the length of time which the fertiliser lay in the soil, but in this case it is likely that reduction in competition from soil micro-organisms was the key factor. Therefore, by delaying the application of some of the NH_4-N fertiliser until tillering meant that there was more competition from the better developed plant roots reducing the availability of the fertiliser nitrogen for immobilisation. This was confirmed by the fact that there was a greater uptake of labelled nitrogen at harvest from the second ammonium split application (Section 4.5.2).

The percentage recovery of fertiliser nitrogen applied is shown in Table 4.4. At both Bush and Lintlaw the recovery of ammonium sulphate rose with increased fertiliser applications. Ammonium nitrate remained generally

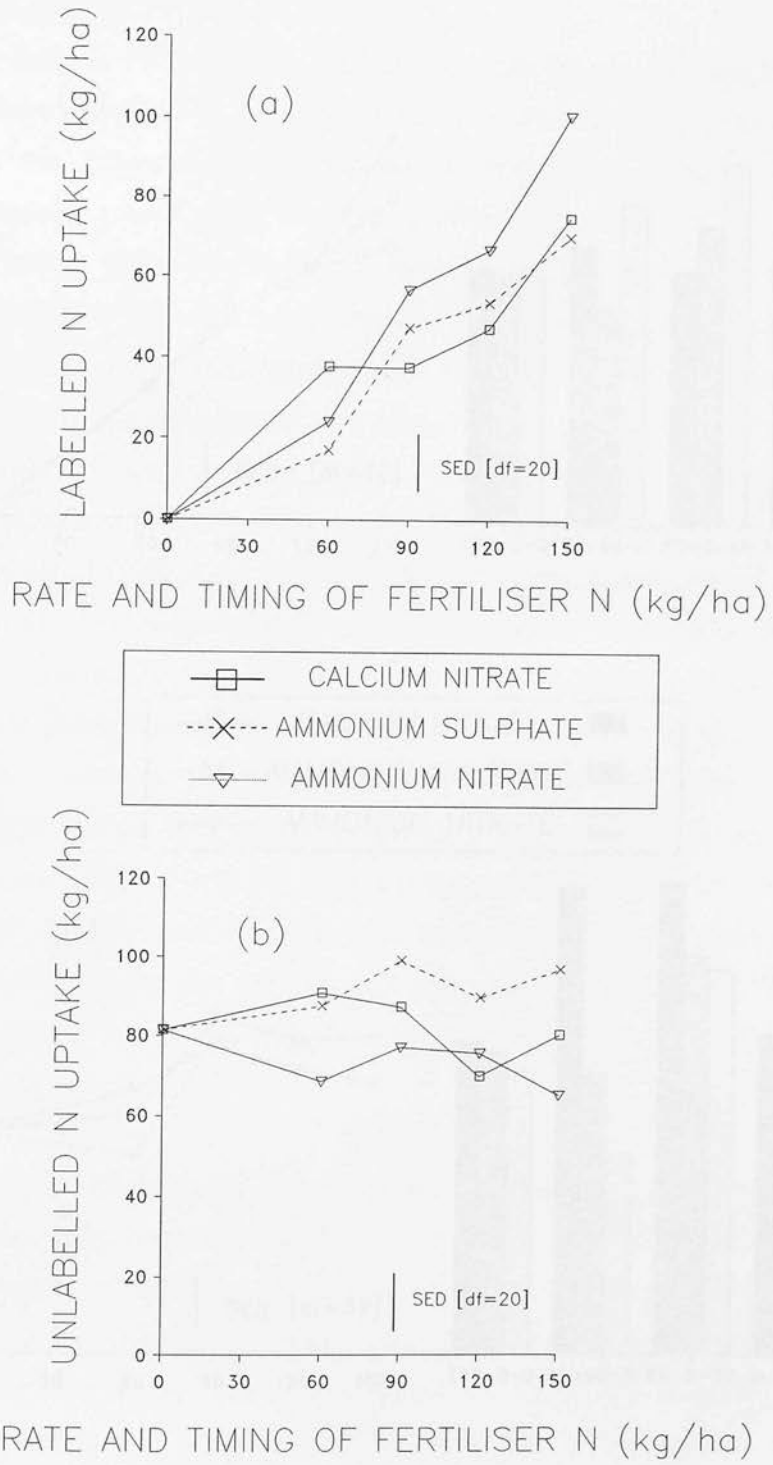


Figure 4.5. Uptake of (a) labelled and (b) unlabelled nitrogen in above ground plant tissue by spring barley as influenced by the rate of fertiliser nitrogen applications, harvest, Bush (Seafield) 1987

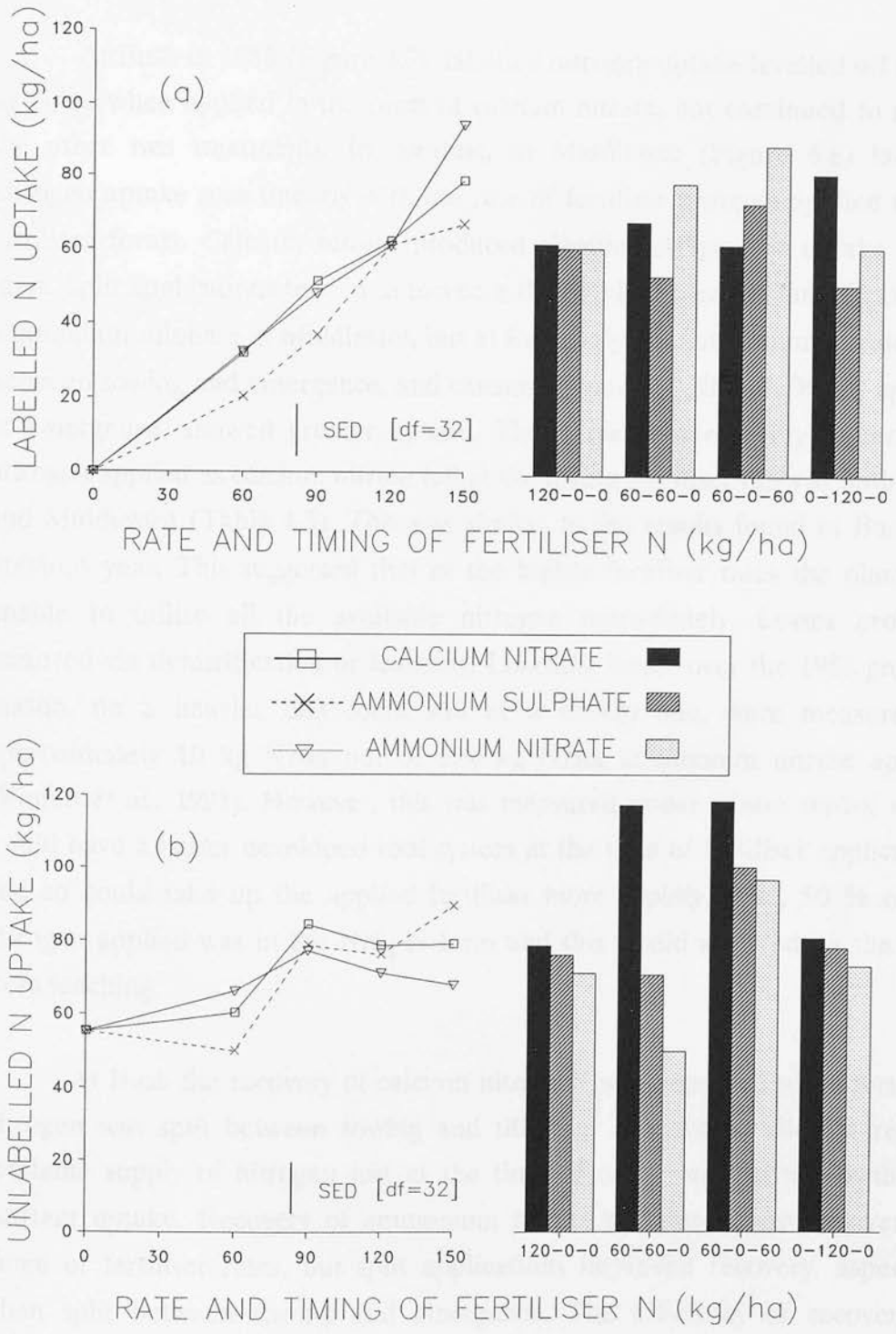


Figure 4.6. Uptake of (a) labelled and (b) unlabelled nitrogen in above ground plant tissue by spring barley as influenced by the rate and timing of fertiliser nitrogen applied, harvest, Lintlaw 1987

constant with only a slight rise in efficiency at high fertiliser rates. Recoveries of calcium nitrate fell as fertiliser rates were increased at Bush, but remained constant at Lintlaw. Split applications gave the greatest improvement in uptake efficiency when applied in the ammonium nitrate form.

At Bush in 1988 (Figure 4.7), labelled nitrogen uptake levelled off at 120 kg N/ha when applied in the form of calcium nitrate, but continued to rise in the other two treatments. In contrast, at Middlestot (Figure 4.8) labelled nitrogen uptake rose linearly with the rate of fertiliser nitrogen applied for all fertiliser forms. Calcium nitrate produced significantly greater uptake at all rates. Split applications tended to increase the uptake of ammonium nitrate and ammonium sulphate at Middlestot, but at Bush only the ammonium nitrate split between sowing and emergence, and calcium nitrate at 120 kg N/ha all applied at emergence, showed greater uptake. The percentage recovery of fertiliser nitrogen applied as calcium nitrate fell at the higher fertiliser rates at both Bush and Middlestot (Table 4.5). This was similar to the results found at Bush the previous year. This suggested that at the higher fertiliser rates the plant was unable to utilise all the available nitrogen immediately. Losses probably occurred via denitrification or leaching. Leaching losses over the 1988 growing season, on a heavier clay loam soil at a nearby site, were measured at approximately 10 kg N/ha out of 120 kg N/ha ammonium nitrate applied (Vinten *et al.*, 1991). However, this was measured under winter barley which would have a better developed root system at the time of fertiliser application, and so could take up the applied fertiliser more rapidly. Also, 50 % of the nitrogen applied was in the NH_4-N form and this would also reduce the risks from leaching.

At Bush the recovery of calcium nitrate N was improved when fertiliser nitrogen was split between sowing and tillering. This would allow a readily available supply of nitrogen just at the time of rapid vegetative growth and nutrient uptake. Recovery of ammonium nitrate remained constant over the range of fertiliser rates, but split applications improved recovery, especially when split between sowing and emergence. The efficiency of recovery of ammonium sulphate improved as fertiliser rates increased. This also occurred in

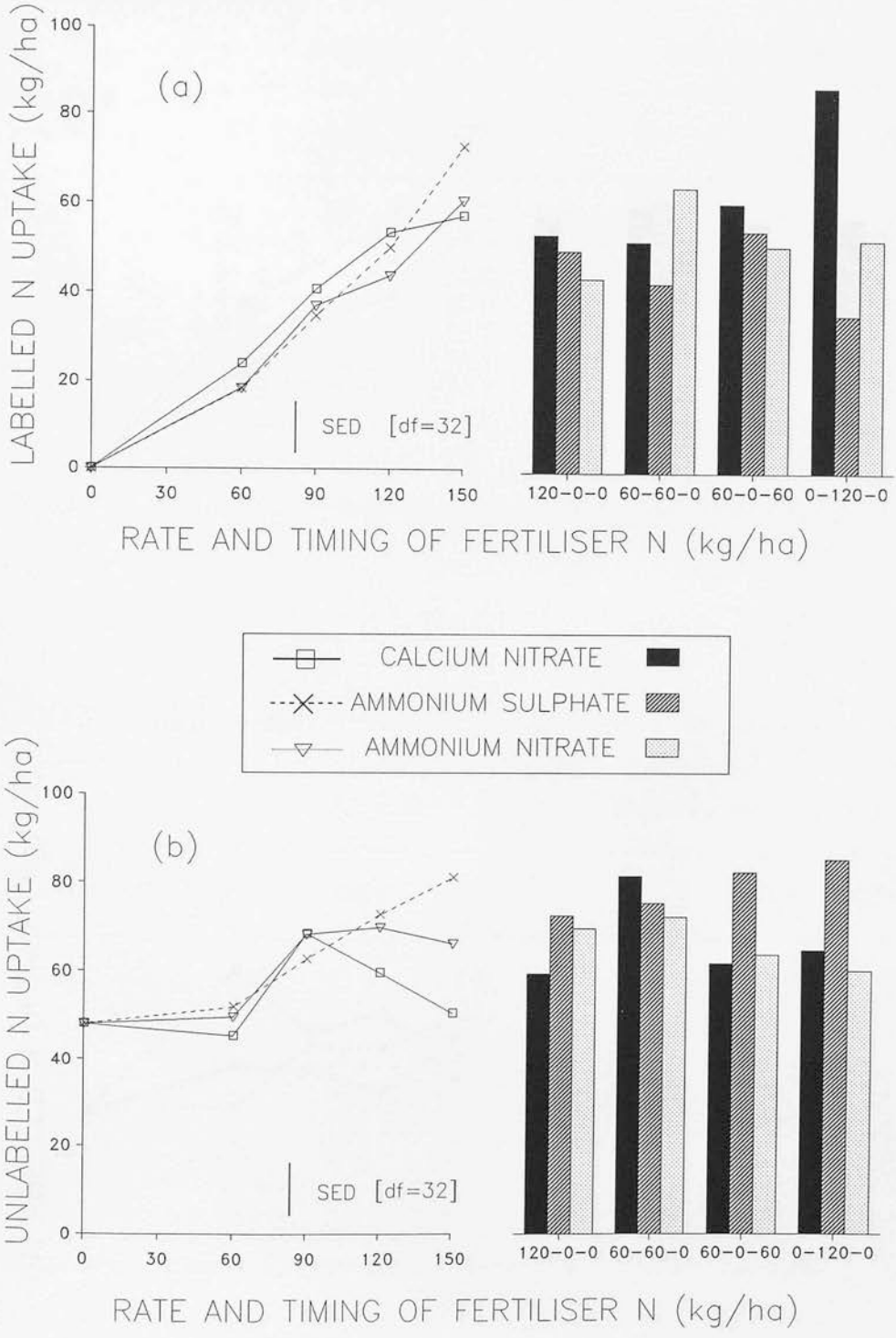


Figure 4.7. Uptake of (a) labelled and (b) unlabelled nitrogen in above ground plant tissue by spring barley as influenced by the rate and timing of fertiliser nitrogen applied, harvest, Bush (Lower Fulford) 1988

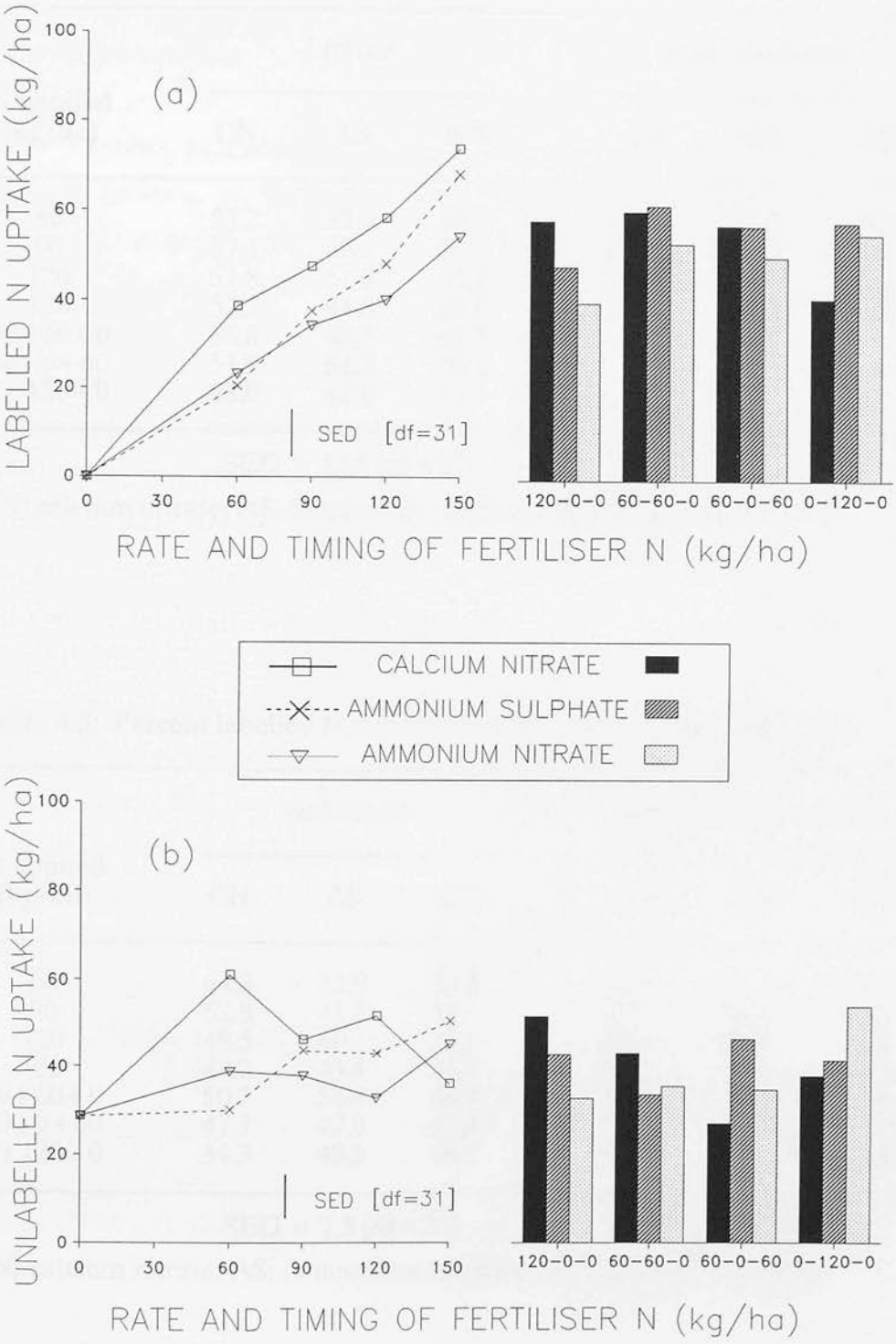


Figure 4.8. Uptake of (a) labelled and (b) unlabelled nitrogen in above ground plant tissue by spring barley as influenced by the rate and timing of fertiliser nitrogen applied, harvest, Middlestot 1988

Table 4.4: Percent labelled N recovery in plant shoots at two sites, 1987

N applied (kg/ha)	Lintlaw			Bush (Seafield)		
	CN	AS	AN	CN	AS	AN
60	53.2	33.9	54.2	62.6	28.2	40.0
90	57.1	40.9	53.7	41.7	52.6	63.0
120	51.8	51.0	51.0	39.4	44.7	55.6
150	52.5	44.6	63.0	50.0	46.7	67.3
60+60+0	56.8	44.7	65.7	--	--	--
60+0+60	51.9	61.2	74.5	--	--	--
0+120+0	68.0	42.8	51.1	--	--	--
	SED = 13.5 [df=27]			SED = 12.8 [df=16]		

CN: calcium nitrate; AS: ammonium sulphate; AN: ammonium nitrate

Table 4.5: Percent labelled N recovery in plant shoots at two sites, 1988

N applied (kg/ha)	Middlestot			Bush (Lower Fulford)		
	CN	AS	AN	CN	AS	AN
60	64.3	33.9	38.6	40.0	30.5	30.7
90	52.8	41.8	38.1	45.3	38.6	41.2
120	48.5	40.1	33.5	44.6	41.7	36.6
150	49.2	45.4	36.1	38.1	48.5	40.4
60+60+0	50.3	51.4	44.4	43.4	35.7	53.5
60+0+60	47.7	47.7	41.9	50.6	45.5	42.7
0+120+0	34.3	48.3	46.1	72.4	29.9	43.9
	SED = 7.3 [df=27]			SED = 10.2 [df=28]		

CN: calcium nitrate; AS: ammonium sulphate; AN: ammonium nitrate

1987, and could be due to the lower mobility of NH_4-N in the soil. This would reduce the movement of nutrients down the soil profile with surface applied fertiliser (Section 5.1.3). Therefore fertiliser nitrogen would still be accumulated near the soil surface and not well distributed near the developing roots. At higher fertiliser rates sufficient NH_4-N may be present to at least partially offset the reduced mobility.

Another possible explanation for the reduced recovery of ammonium sulphate fertiliser at low application rates is that the recovery of fertiliser nitrogen, as determined by ^{15}N, was reduced by 'pool substitution' (Jenkinson *et al.*, 1985; Hart *et al.*, 1986). Pool substitution has been shown to have a proportionately greater effect on low fertiliser ^{15}N additions compared to higher application rates (Jenkinson *et al.*, 1985). They also showed that a delay in the uptake of nitrogen after application would enhance the effect of pool substitution. For the first few weeks after sowing there was little uptake of nitrogen in the plant as there was not yet a sufficiently developed root system in the young barley plants. Therefore, there was more time for the ^{15}N-labelled fertiliser to be immobilised and replaced with mineralised ^{14}N from the soil organic nitrogen pool before it was taken up by the plant. Other research has shown that the effect of pool substitution is greater when working with $^{15}NH_4$-N rather than $^{15}NO_3$-N (Kowalenko and Cameron, 1978; Steele *et al.*, 1980). This is because the pool substitution is regulated by the rate of immobilisation by micro-organisms in the soil, (Jenkinson *et al.*, 1985) whose preference for NH_4-N as a substrate is well documented.

In 1989 the recovery of labelled nitrogen was significantly influenced by the form in which the fertiliser was applied (Figures 4.9 and 4.10). At both sites uptake was lower when applied in the ammonium form compared to the nitrate form. Splitting the fertiliser application increased the uptake of labelled nitrogen in the calcium nitrate treatments at Upper Cairnie. The efficiency of recovery was generally high (Table 4.6), especially at the Bush site. At Bush the nitrate fertiliser treatments gave the highest recoveries, with the greatest efficiency at 60 kg N/ha fertiliser applied. At all rates above this, whether applied as a single or split treatment, percentage recovery did not vary

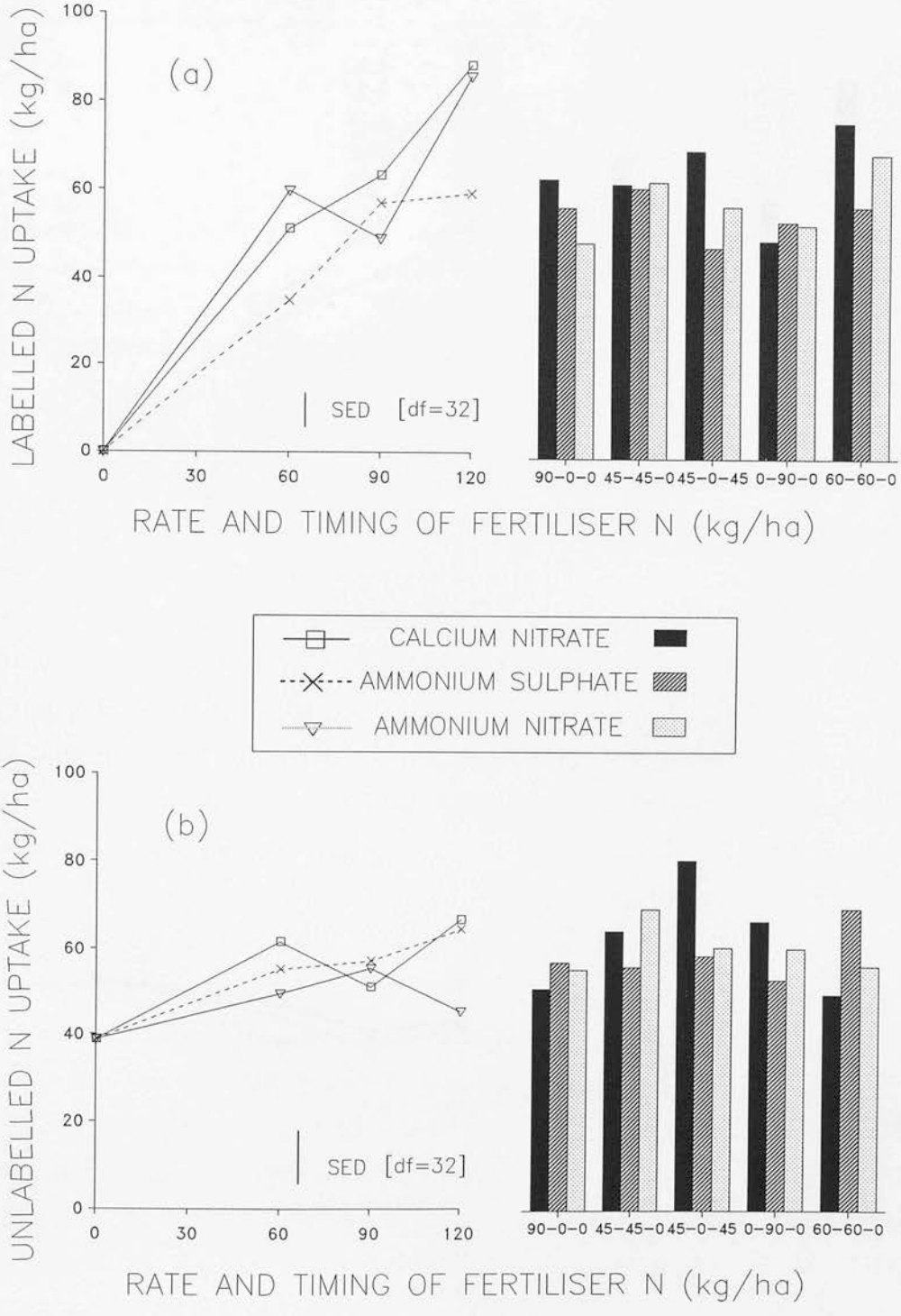


Figure 4.9. Uptake of (a) labelled and (b) unlabelled nitrogen in above ground plant tissue by spring barley as influenced by the rate and timing of fertiliser nitrogen applied, harvest, Bush (March Park) 1989

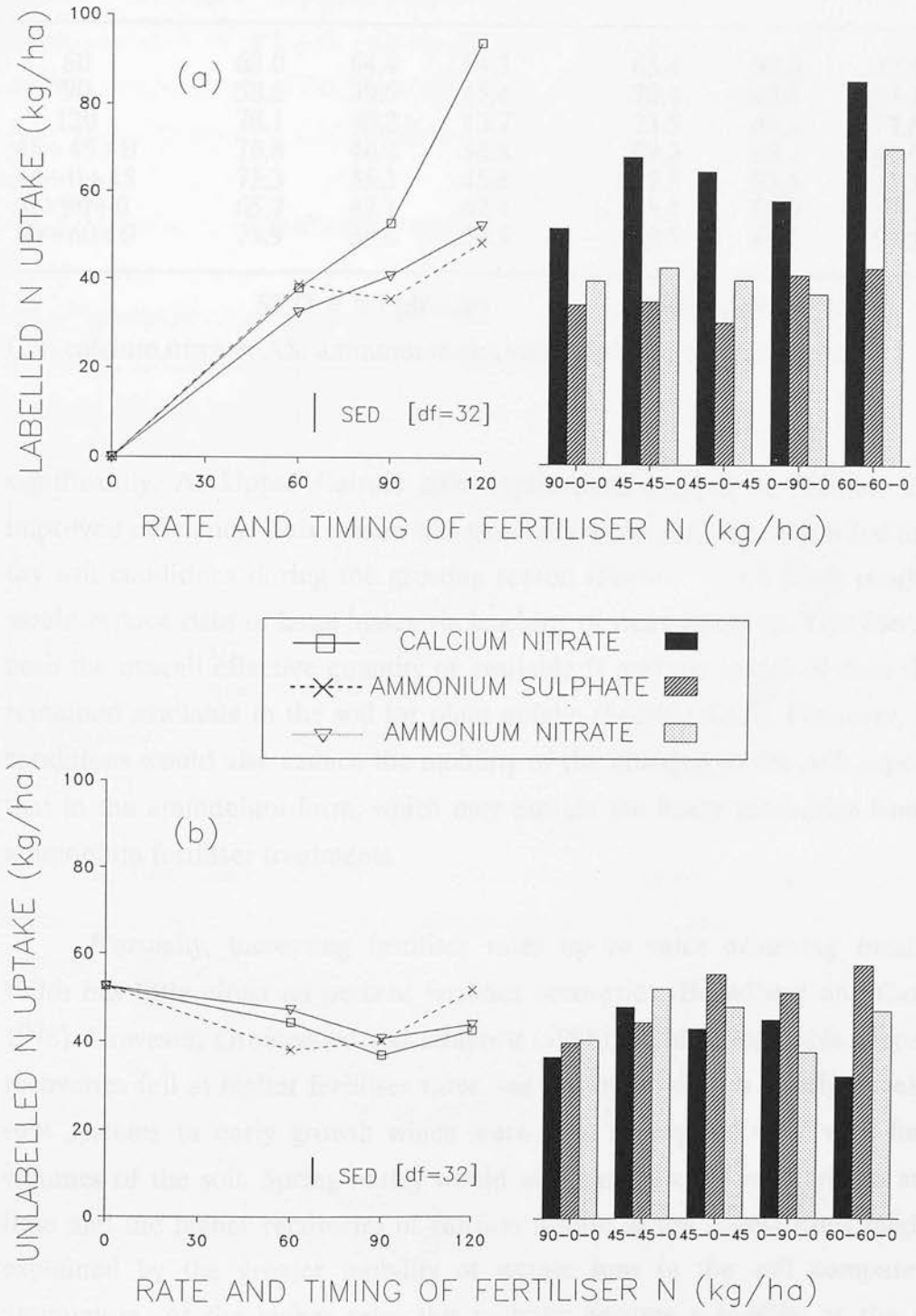


Figure 4.10. Uptake of (a) labelled and (b) unlabelled nitrogen in above ground plant tissue by spring barley influenced by the rate and timing of fertiliser nitrogen applied, harvest, Upper Cairnie 1989

Table 4.6: Percent labelled N recovery in plant shoots at two sites, 1989

N applied (kg/ha)	Upper Cairnie			Bush (March Park)		
	CN	AS	AN	CN	AS	AN
60	63.0	64.4	54.3	85.4	58.0	82.9
90	58.6	39.5	45.4	70.4	63.4	54.7
120	78.1	40.2	43.7	73.5	49.4	71.6
45+45+0	76.8	40.4	48.8	69.2	68.1	69.6
45+0+45	73.3	35.3	45.8	77.5	53.6	63.7
0+90+0	65.7	47.1	42.4	55.4	59.9	59.2
60+60+0	71.9	36.6	59.5	63.5	47.7	57.5
	SED = 9.7 [df=28]			SED = 11.4 [df=28]		

CN: calcium nitrate; AS: ammonium sulphate; AN: ammonium nitrate

significantly. At Upper Cairnie split applications applied as calcium nitrate improved efficiency. This season was generally warm and dry, which led to very dry soil conditions during the growing season (Section 5.1.6). Such conditions would reduce risks of large losses via leaching or denitrification. This increased both the overall effective quantity of available N and the length of time that it remained available in the soil for plant uptake (Section 5.1.6). However, these conditions would also reduce the mobility of the nitrogen in the soil, especially that in the ammonium form, which may explain the lower recoveries from the ammonium fertiliser treatments.

Normally, increasing fertiliser rates up to rates achieving maximum yields has little effect on percent fertiliser recoveries (Broadbent and Carlton, 1978). However, Greenwood and Draycott (1988) found in vegetable crops that recoveries fell at higher fertiliser rates and attributed this to poorly developed root systems in early growth which were able to explore only very limited volumes of the soil. Spring barley would also have a small root system at this time and the higher recoveries of calcium nitrate at the lowest rates might be explained by the greater mobility of nitrate ions in the soil compared to ammonium. At the higher rates this mobility became a liability as the roots

could not utilise all the available nitrate and so there was a greater potential for leaching and denitrification. In winter cereals this does not occur, due to an already well established root system able to utilise immediately much more of the fertiliser nitrogen applied. Another possible explanation for the increased recovery at higher fertiliser rates of ammonium sulphate could be the immobilisation of NH_4-N initially into the biomass from where it is quite quickly released again (Bristow *et al.*, 1987), but which would allow the crop sufficient time to develop a more extensive root system.

4.2.2: Uptake of unlabelled nitrogen

The uptake of unlabelled nitrogen did not show the same linear rise as the uptake of labelled nitrogen at any of the sites. At Bush in 1987 (Figure 4.5) both calcium nitrate and ammonium nitrate fertiliser forms showed a constant uptake of between 70 kg N/ha and 80 kg N/ha at all rates of fertiliser applied. There was a slight rise in the uptake of unlabelled nitrogen when the fertiliser was applied in the form of ammonium sulphate. There was a similar rise in uptake from treatments when ammonium sulphate fertiliser was applied at Lintlaw 1987 (Figure 4.6). Unlabelled nitrogen uptake was also greater in the calcium nitrate treatments at fertiliser rates of 90 kg N/ha and above. Split applications also increased unlabelled nitrogen uptake in the calcium nitrate treatments.

In 1988 the uptake of unlabelled nitrogen in the calcium nitrate and ammonium nitrate treatments remained constant at all rates above 60 kg N/ha at Bush (Figure 4.7), and at all rates above zero at Middlestot (Figure 4.8). The uptake of unlabelled nitrogen in the ammonium sulphate treatments increased steadily with increased fertiliser applications at Bush. Splitting fertiliser applications had little effect on the uptake of unlabelled nitrogen.

In 1989, uptake remained constant at all fertiliser rates except for the zero application rate at Bush (Figure 4.9). Once again split fertiliser applications had little effect, with the exception of the calcium nitrate treatment splitting 90 kg N/ha between sowing and tillering at Bush.

In general, the lack of evidence of a steady increase in the uptake of unlabelled nitrogen with increased fertiliser applications, for most treatments, suggested that there was no real "priming" effect as proposed by previous research (Broadbent and Nakashima, 1971; Westerman and Kurtz, 1974). The only real evidence of any effect occurred with the ammonium sulphate treatments. Another explanation put forward to explain increases in the uptake of unlabelled nitrogen measured in some trials, is that it is only an apparent effect (Jenkinson *et al.*, 1985). This effect, called the "added nitrogen interaction" (ANI) occurs in trials using ^{15}N-labelled fertiliser, and is caused by the continuous mineralisation-immobilisation turnover of nitrogen in the soil. Research carried out under field conditions (Jansson, 1958; Aulakh and Rennie, 1984; Recous *et al.*, 1988a) and in the laboratory (Okereke and Meints, 1985) has shown that there is preferential immobilisation of NH_4-N by soil micro-organisms. Thus the greater uptake of unlabelled nitrogen at the higher rates of ammonium sulphate fertiliser applications may be attributable to the greater likelihood of immobilisation of NH_4-N than NO_3-N by the soil microbes, resulting in a greater pool-substitution effect on the ^{15}N fertiliser added. The fact that there was no such effect with the ammonium sulphate treatment at Upper Cairnie could be explained by the fact that the ANI effect requires good interaction between the ^{15}N fertiliser applied and the unlabelled inorganic nitrogen already present in the soil (Jenkinson *et al.*, 1985). Soil conditions were very dry at Upper Cairnie; this would have had the effect of reducing the mobility of the NH_4-N and may have prevented a complete interaction with the unlabelled nitrogen in the soil, thus reducing any ANI effect. The lack of an ANI due to a lack of interaction between the two nitrogen pools has also been observed by other workers (Hart *et al.*, 1986; Nielsen *et al.*, 1988; Recous *et al.*, 1988b).

The data for the calcium nitrate and ammonium nitrate treatments showed that uptake remained constant at all rates of applied fertiliser, but that uptake was slightly lower when no fertiliser nitrogen was applied. This could have been caused by a stimulation in plant growth, including roots, by the lowest rate of fertiliser which would allow greater exploration of the soil and greater uptake of unlabelled nitrogen, as proposed by Sørensen (1982). Under field

conditions in Scotland (Smith *et al.*, 1984) it was concluded that the constant uptake of soil nitrogen with increasing fertiliser rates was due to efficient root exploration at the lower fertiliser rates in spring barley grown on a loamy sand soil. This was in contrast to results from a heavier badly structured soil, where the lower uptake of soil nitrogen at low fertiliser rates was attributed to restricted root growth at these lower rates, observed earlier at this site (Holmes, 1976; Pidgeon, 1980).

A study of the uptake of both labelled and unlabelled nitrogen at all six sites studied between 1987 and 1989 showed that there was considerable variation in the uptake of unlabelled nitrogen (Figure 4.11). Average uptake ranged from 40 kg N/ha at Middlestot to 82 kg N/ha at Bush in 1987. Even in the same season there were considerable differences. This variation in the uptake of unlabelled nitrogen was much greater than the variation in the efficiency of uptake of labelled nitrogen, which ranged from 43 % at Bush in 1988 to 61 % at Bush in 1989.

The variation in the uptake of unlabelled nitrogen occurred on soils which, with the exception of Upper Cairnie, were all classed as low nitrogen soils (N-Index Zero) on the basis of previous cropping. From these results it appeared that changes in fertiliser form, or timing of application, had relatively little effect on overall nitrogen uptake compared to the variation due to the uptake of native soil nitrogen between different sites.

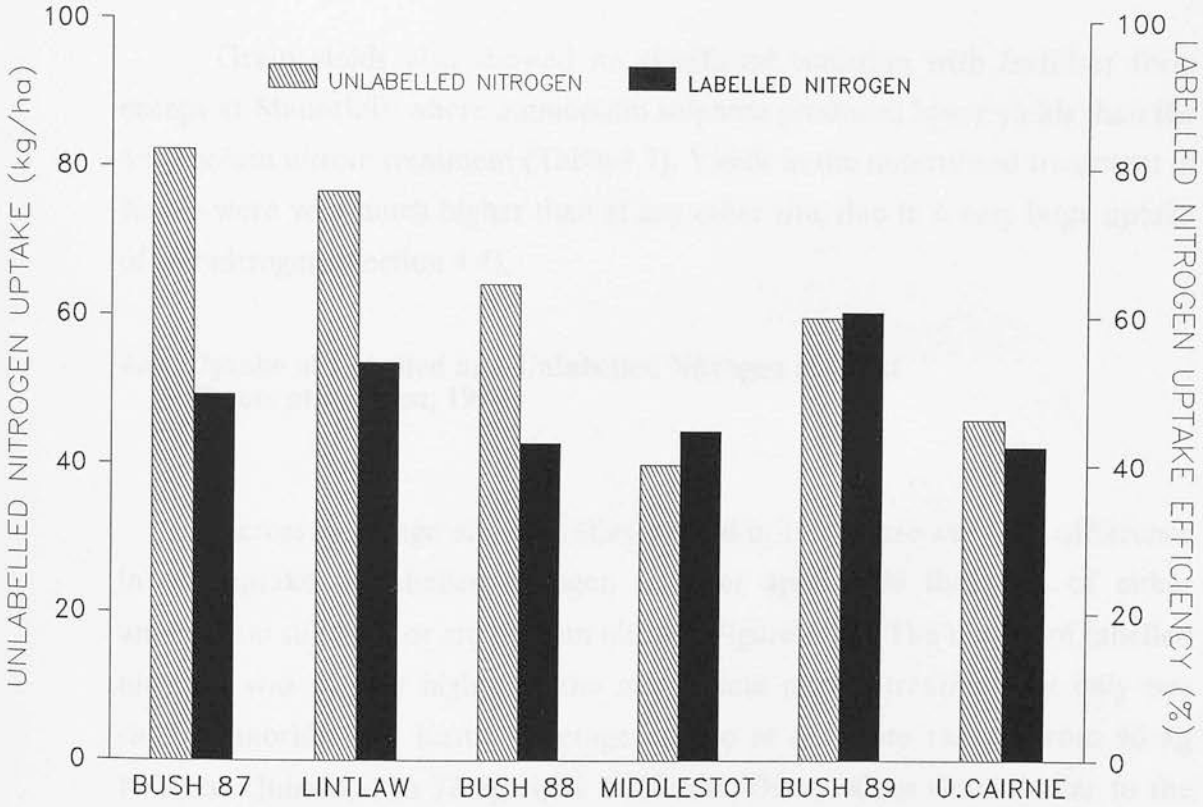


Figure 4.11. Mean uptake of labelled and unlabelled nitrogen in above ground plant tissue in spring barley over a range of fertiliser nitrogen applications at 6 sites, harvest, 1987-1989

4.3: Grain Nitrogen Content and Yield, 1990

In 1990 the site effect was further investigated with trials laid out at six different sites. Details of the sites are given in Table 3.3. Figure 4.12 shows the grain nitrogen contents for each fertiliser nitrogen treatment applied at each site. All the sites, with the exception of Kettle, had been previously cropped with cereals and yet grain nitrogen contents still ranged from 1.4 % to 1.8 % N with 120 kg N/ha fertiliser applied at sowing. Once again, site had a much greater effect than the form of fertiliser applied.

Grain yields also showed no significant variation with fertiliser form except at Manorhill, where ammonium sulphate produced lower yields than the ammonium nitrate treatment (Table 4.7). Yields in the unfertilised treatment at Kettle were very much higher than at any other site, due to a very large uptake of soil nitrogen (Section 4.4).

4.4: Uptake of Labelled and Unlabelled Nitrogen in Plant Shoots at Harvest, 1990

Across the range of the six sites studied in 1990 there was little difference in the uptake of labelled nitrogen fertiliser applied in the form of either ammonium sulphate or ammonium nitrate (Figure 4.13). The uptake of labelled nitrogen was slightly higher in the ammonium nitrate treatment at only two sites, Manorhill and Kettle. Average uptake at each site ranged from 46 kg N/ha at Quixwood to 73 kg N/ha at Kettle. These values were similar to the uptake of labelled nitrogen in the same treatments in the previous seasons.

Unlabelled nitrogen uptake in 1990 showed no effect of fertiliser form, except at Manorhill, where uptake was greater in the ammonium nitrate fertiliser treatment (Figure 4.14). Uptake was significantly lower at all sites when no fertiliser was applied with the exception of Kettle where uptake was higher in the unfertilised treatments. This site differed from the other sites that year in that the previous crop was brussels sprouts rather than a cereal, and thus

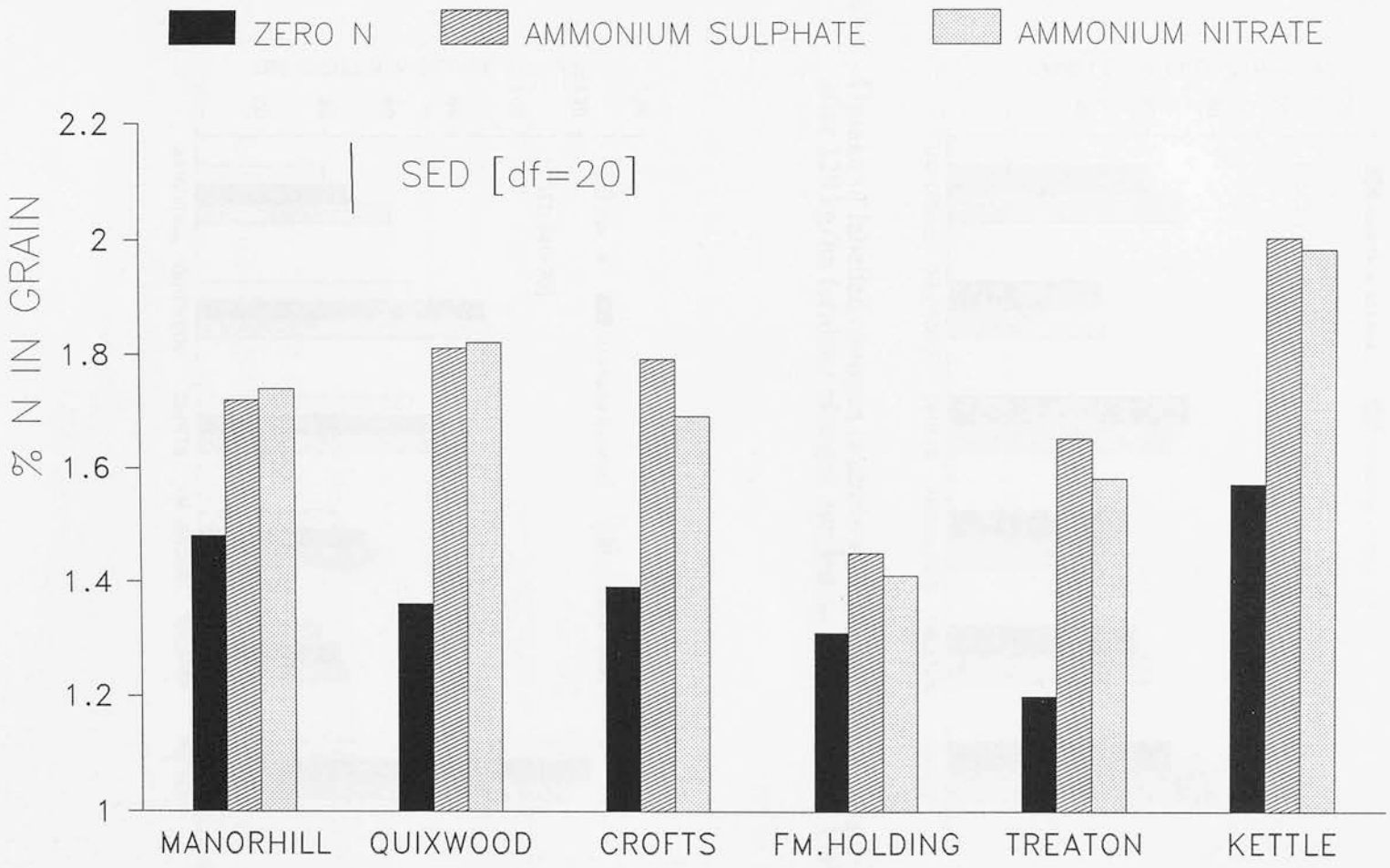


Figure 4.12. Nitrogen concentration in the grain (%) in spring barley at fertiliser rates of zero and 120 kg N/ha at six sites, harvest, 1990

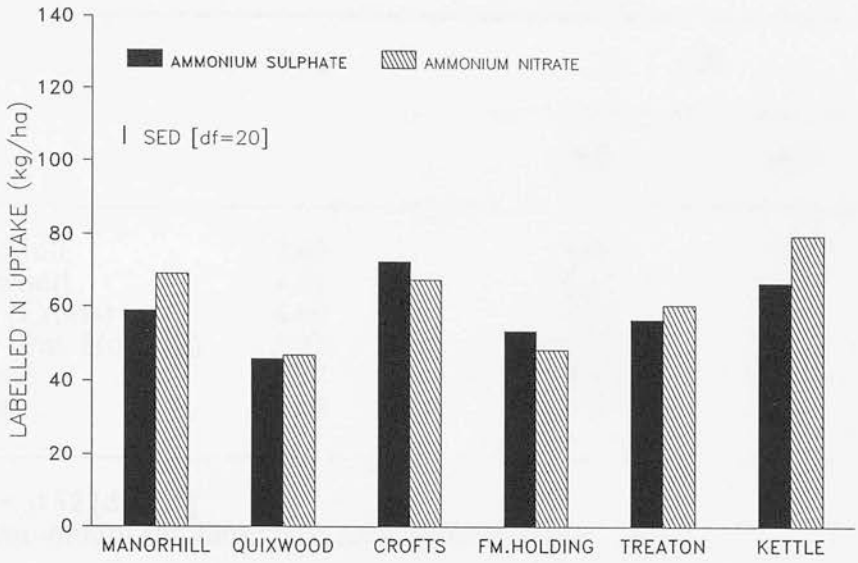


Figure 4.13. Uptake of labelled nitrogen in above ground plant tissue in spring barley after 120 kg/ha fertiliser nitrogen applied, at 6 sites, harvest, 1990

Figure 4.14. Uptake of unlabelled nitrogen in above ground plant tissue in spring barley after zero or 120 kg/ha fertiliser nitrogen applied, at 6 sites, harvest, 1990

Table 4.7: Grain yields (t/ha, 15 % moisture) as affected by fertiliser nitrogen application at two sites, 1990

Site	Fertiliser applied (kg N/ha)		
	Zero	120	
		AS	AN
Manorhill	2.45	4.85	6.09
Quixwood	4.31	6.13	6.19
Bush (Crofts)	4.60	7.38	7.76
Bush (Fm. Holding)	3.33	6.78	7.10
Treaton	2.87	5.82	6.19
Kettle	6.68	7.30	7.35

SED = 0.52 [df=18]
AS: ammonium sulphate; AN: ammonium nitrate

the soil was categorised as N-Index = 1 (MAFF, 1985). Total uptake of unlabelled nitrogen was much higher than any of the other sites with an average uptake of 123 kg N/ha. Grain yields were also significantly higher at Kettle, with the greatest increase compared to other sites being found in zero nitrogen treatments (Section 4.3). This indicated that there was a plentiful supply of native soil nitrogen which the crop could take up. One source of this soil nitrogen was likely to be from the mineralisation of the residues of the previous crop rather than from older soil organic matter fractions; the soil had, in fact a low organic matter content of 2.8 % (Table 3.3). There may also have been some uptake of nitrate from further down the soil profile. In two of the previous four seasons vegetable crops were grown on the site, which was part of an intensive horticultural farm. It is likely that large amounts of nitrate fertiliser would have been applied, and that significant proportions of this might have leached down the soil profile, which had a loamy sand texture. It is possible that there was uptake of soil nitrogen from these deeper soil layers. In the zero plots such enhanced nitrogen availability could have reduced the relative benefit gained by fertilised crops in terms of greater root growth and nitrogen availability.

The other five sites had all been previously cropped with a cereal, and yet the average unlabelled nitrogen uptake at each site ranged from 41 kg N/ha at Treaton to 79 kg N/ha at Quixwood (Figure 4.15). This variation between sites was greater than the variation in labelled nitrogen uptake which ranged from 48 kg N/ha at Quixwood to 70 kg N/ha at Crofts. At Kettle, where grain yields and unlabelled nitrogen uptake were much higher than the other sites, labelled nitrogen uptake was only slightly higher at 73 kg N/ha. These results confirmed findings from the previous seasons.

4.5: Uptake of Labelled and Unlabelled Nitrogen in Plant Shoots over the Growing Season, 1987-1989

In this section the uptake of labelled and unlabelled nitrogen in plant shoots over the growing season is discussed. Representative diagrams are presented in the main text, with the remaining diagrams to be found in the appendix.

4.5.1: Bush (Seafield) 1987

At this site, the uptake of labelled nitrogen, applied at a rate of 120 kg N/ha as either calcium nitrate or ammonium nitrate, rose steadily from 47 to 75 days after sowing during the period of stem elongation, reaching a maximum amount before anthesis of 70 kg N/ha and 78 kg N/ha respectively. When applied in the form of ammonium sulphate, uptake continued to rise for a further two weeks. However, maximum uptake of labelled nitrogen in the ammonium sulphate treatment, at 65 kg N/ha, was still lower than in the other treatments, due to a less steep rise in uptake during stem elongation. In all three treatments the amount of labelled nitrogen in the plant tissues fell by harvest, most notably in the calcium nitrate treatment, falling from 70 kg N/ha after 75 days to 47 kg N/ha at harvest. The uptake of unlabelled nitrogen was much lower than that of labelled nitrogen prior to anthesis, but continued to rise until the plants were harvested at the end of the growing season. These effects were comparable with the results reported for spring barley grown in Scotland in similar environmental conditions by Smith *et al.* (1984).

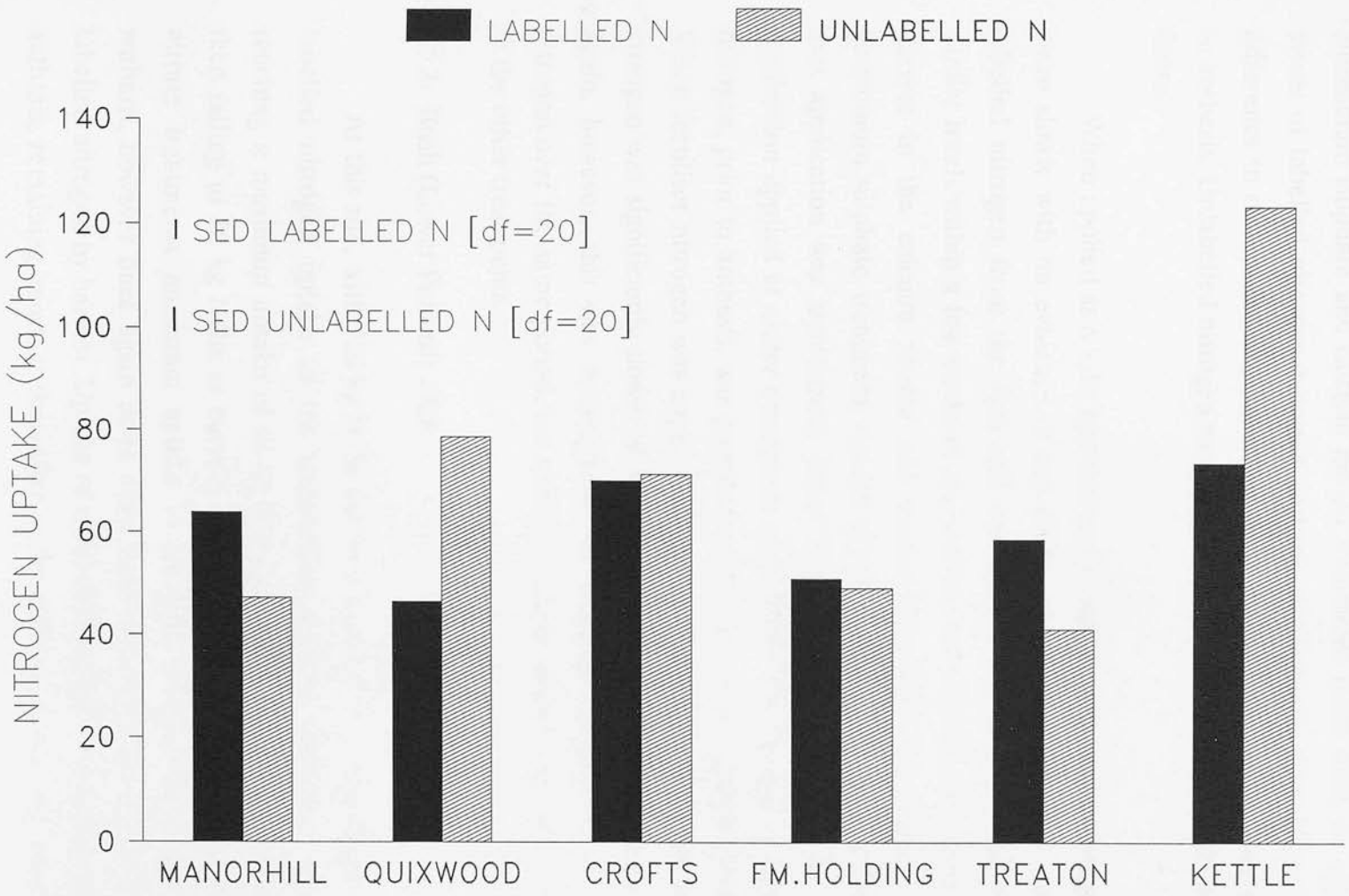


Figure 4.15. Mean uptake of labelled and unlabelled nitrogen in above ground plant tissue in spring barley at six sites, harvest, 1990

4.5.2: Lintlaw 1987

Here, the uptake of labelled nitrogen, with 120 kg N/ha fertiliser applied at sowing, followed a similar pattern to the Bush site, except that in the ammonium sulphate and calcium nitrate treatments there were no significant losses of labelled nitrogen between anthesis and harvest. Also, there was no difference in the uptake of labelled nitrogen between the fertiliser forms prior to anthesis. Unlabelled nitrogen rose continuously until harvest for all fertiliser forms.

When applied as a split-application the uptake of labelled nitrogen rose more slowly with no evidence of any decline before harvest. The uptake of labelled nitrogen from the first and second split applications had reached similar levels within a few weeks of application, and this was maintained up to harvest in the calcium nitrate and ammonium nitrate treatments. In the ammonium sulphate treatment, uptake of labelled nitrogen derived from the first application was significantly lower than that derived from the second application applied at either emergence or tillering. The uptake of unlabelled nitrogen, prior to anthesis, was greater in the ammonium sulphate treatments. When fertiliser nitrogen was applied all at emergence, the uptake of labelled nitrogen was significantly slower in the ammonium sulphate treatments. Once again, however, this was accompanied by a greater uptake of unlabelled nitrogen over the same period, but overall nitrogen uptake was still lower than in the other treatments.

4.5.3: Bush (Lower Fulford) 1988

At this site, with 120 kg N/ha fertiliser applied at sowing (Figure 4.16) labelled nitrogen uptake in the ammonium sulphate treatment was slow, reaching a maximum uptake of 64 kg N/ha several weeks after anthesis and then falling to 50 kg N/ha at harvest. In the calcium nitrate and ammonium nitrate treatments maximum uptake of labelled nitrogen occurred before anthesis, however once again there were losses of more than 25 kg N/ha of labelled nitrogen by harvest. Uptake of unlabelled nitrogen stopped rising after anthesis, remaining constant thereafter in the calcium nitrate and ammonium

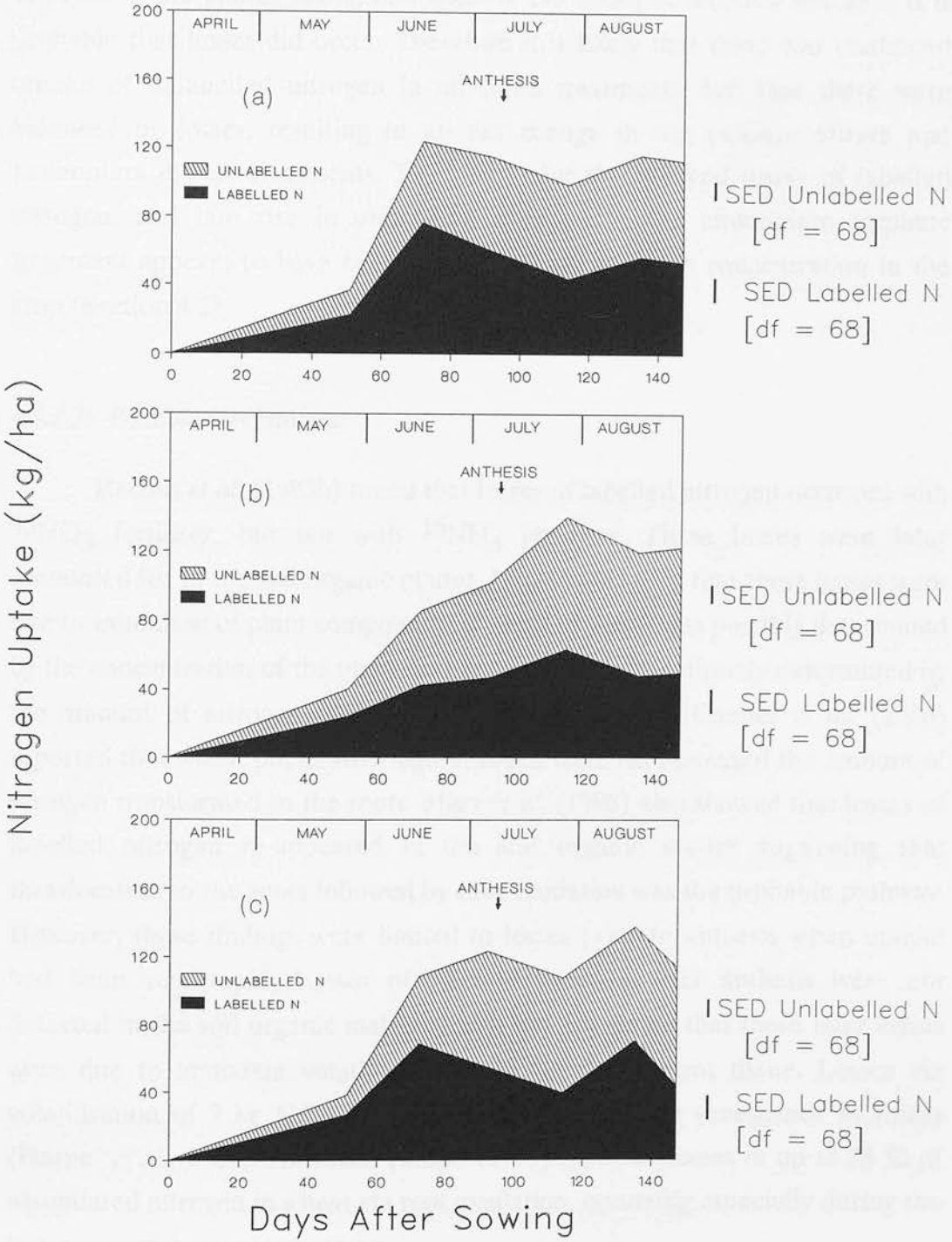


Figure 4.16. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (Lower Fulford) 1988

nitrate treatments. In the ammonium sulphate treatment uptake rose until considerably after anthesis.

Even though there was no observed drop in the amount of unlabelled nitrogen in the plants, taking into account the losses of labelled nitrogen, it is probable that losses did occur. Therefore it is likely that there was continued uptake of unlabelled nitrogen in all three treatments, but that these were balanced by losses, resulting in no net change in the calcium nitrate and ammonium nitrate treatments. The reason for the reduced losses of labelled nitrogen, and late rise in unlabelled nitrogen in the ammonium sulphate treatment appears to have been due to a lower nitrogen concentration in the crop (Section 4.2).

4.5.3.1: Possible mechanisms

Recous *et al.* (1988b) found that losses of labelled nitrogen occurred with $^{15}NO_3$ fertiliser, but not with $^{15}NH_4$ fertiliser. These losses were later accounted for in the soil organic matter. It was concluded that these losses were due to exudation of plant compounds, the rate of which was possibly determined by the concentration of the plant nitrate pool as this was directly determined by the amount of nitrogen taken up in the nitrate form. Cooper *et al.* (1986) reported that wheat plants with high nitrogen contents increased the amount of nitrogen translocated to the roots. Mary *et al.* (1988) also showed that losses of labelled nitrogen re-appeared in the soil organic matter suggesting that translocation to the roots followed by root exudation was the probable pathway. However, these findings were limited to losses prior to anthesis when uptake had been very rapid. Losses of labelled nitrogen after anthesis were not detected in the soil organic matter, and it was suggested that these later losses were due to ammonia volatilisation from senescing plant tissue. Losses via volatilisation of 7 kg N/ha have been measured during senescence in wheat (Harper *et al.*, 1987). However, Janzen (1990) reported losses of up to 33 % of assimilated nitrogen in wheat via root exudation, occurring especially during the latter part of the growing season.

Overall uptake of unlabelled nitrogen was greatest for the ammonium sulphate treatment. During the early part of stem elongation, between 51 and 72 days after sowing, the lower rate of labelled nitrogen uptake was offset by a more rapid uptake of unlabelled nitrogen compared to the other treatments. This may have been due to uptake of more mobile unlabelled soil nitrate at a time of high demand, or it could have been as a result of pool-substitution of applied $^{15}NH_4$-N reducing the apparent fertiliser uptake. Results showing the relative amounts of NH_4-N and NO_3-N in the soil 51 days after sowing (Section 5.1.3) showed that there was still 68 kg NH_4-N/ha present in the soil, indicating that there was considerable scope for pool substitution. There was also a significant amount of NO_3-N present, which indicated that this supply was not limiting. Therefore it would appear that pool substitution was significant.

4.5.3.2: Effect of Splitting

When fertiliser applications were split the uptake of unlabelled nitrogen continued to rise until harvest (Figure 4.17). In the ammonium sulphate treatments, uptake of labelled nitrogen from the first application remained constant after about 70 days, but uptake from the second application continued to rise until shortly before harvest. There was a greater final recovery of labelled nitrogen from the second application. When all the fertiliser was applied at emergence there was a very rapid uptake of labelled nitrogen in the calcium nitrate and ammonium nitrate treatments between 51 and 72 days after sowing. This period of uptake coincided with the start of stem elongation and a large demand for nutrients by the rapidly growing crop. During this period, however, the uptake of unlabelled nitrogen was low and only increased significantly around the time of booting and ear emergence. This coincided with the end of the fall in soil mineral nitrogen, suggesting that the plants had used up all the available fertiliser nitrogen by this time. Uptake of labelled nitrogen in the ammonium sulphate treatment was less rapid, but continued to rise until well after anthesis. Maximum uptake was 62 kg N/ha, lower than the other fertiliser forms, but there was still a loss of 26 kg N/ha by harvest.

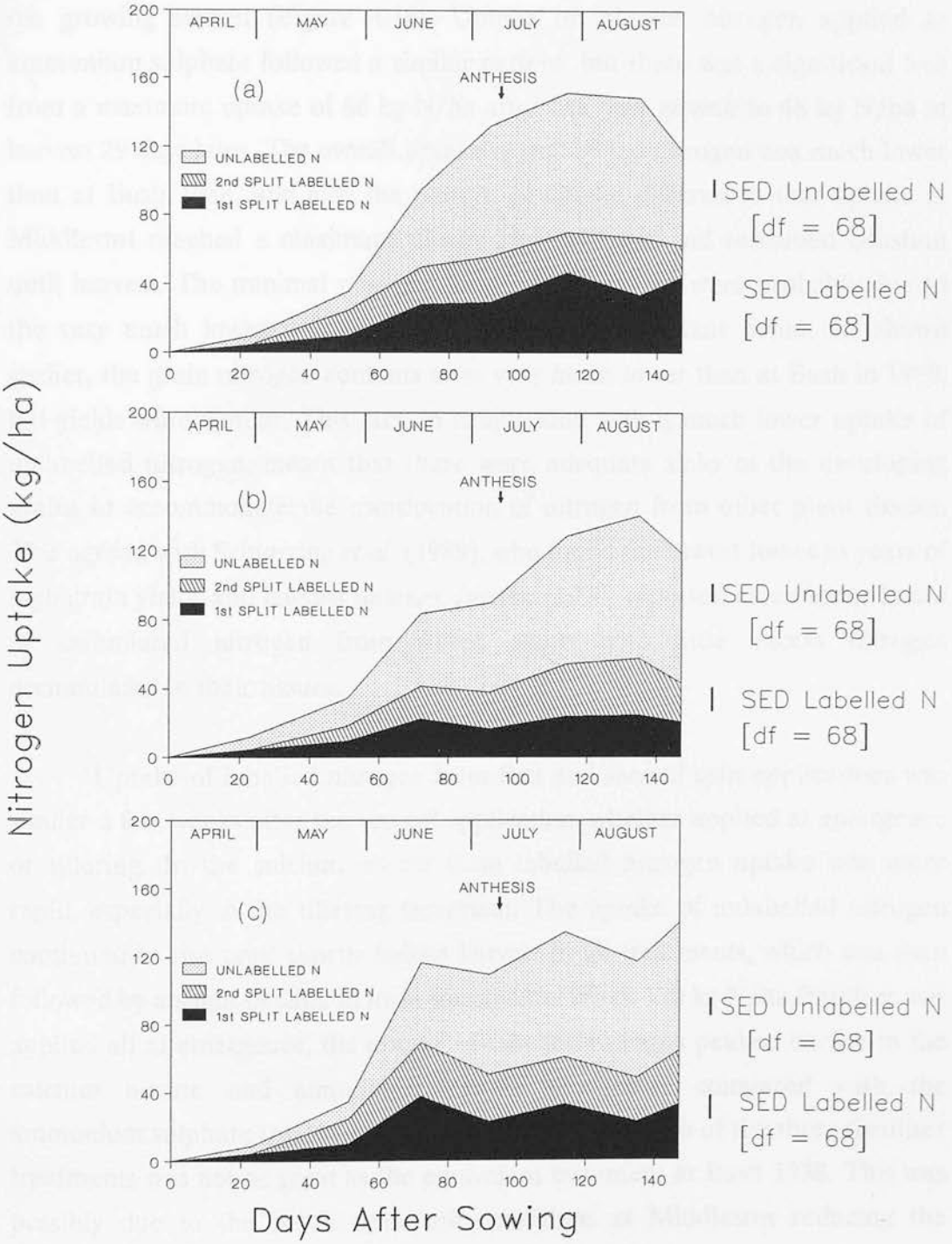


Figure 4.17. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 60 kg/ha at sowing and 60 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (Lower Fulford) 1988

4.5.4: Middlestot 1988

The uptake of seed-bed applied labelled nitrogen in the ammonium nitrate form was less rapid than at Bush 1988, but continued to rise for most of the growing season (Figure 4.18). Uptake of labelled nitrogen applied as ammonium sulphate followed a similar pattern, but there was a significant loss from a maximum uptake of 66 kg N/ha after 128 days growth to 48 kg N/ha at harvest 29 days later. The overall uptake of unlabelled nitrogen was much lower than at Bush 1988, and also the pattern of uptake differed in that uptake at Middlestot reached a maximum shortly after anthesis and remained constant until harvest. The minimal nitrogen losses after anthesis were probably due to the very much lower nitrogen concentrations in the plant tissue. As shown earlier, the grain nitrogen contents were very much lower than at Bush in 1988, but yields were similar. This fact, in conjunction with a much lower uptake of unlabelled nitrogen, meant that there were adequate sinks in the developing grains to accommodate the translocation of nitrogen from other plant tissues. This agreed with Schjørring *et al.* (1989), who found the lowest losses in years of high grain yields and harvest indexes. Janzen (1990) reported much lower losses of assimilated nitrogen from wheat plants with little excess nitrogen accumulated in their tissues.

Uptake of labelled nitrogen from first and second split applications was similar a few weeks after the second application, whether applied at emergence or tillering. In the calcium nitrate form labelled nitrogen uptake was more rapid, especially in the tillering treatment. The uptake of unlabelled nitrogen continued to rise until shortly before harvest in all treatments, which was then followed by a slight decline in most treatments. When 120 kg N/ha fertiliser was applied all at emergence, the uptake of labelled nitrogen peaked earlier in the calcium nitrate and ammonium nitrate treatments compared with the ammonium sulphate treatment. The rate of uptake in each of the three fertiliser treatments was not as great as the equivalent treatment at Bush 1988. This was possibly due to the much drier soil conditions at Middlestot reducing the mobility of the applied nitrogen.

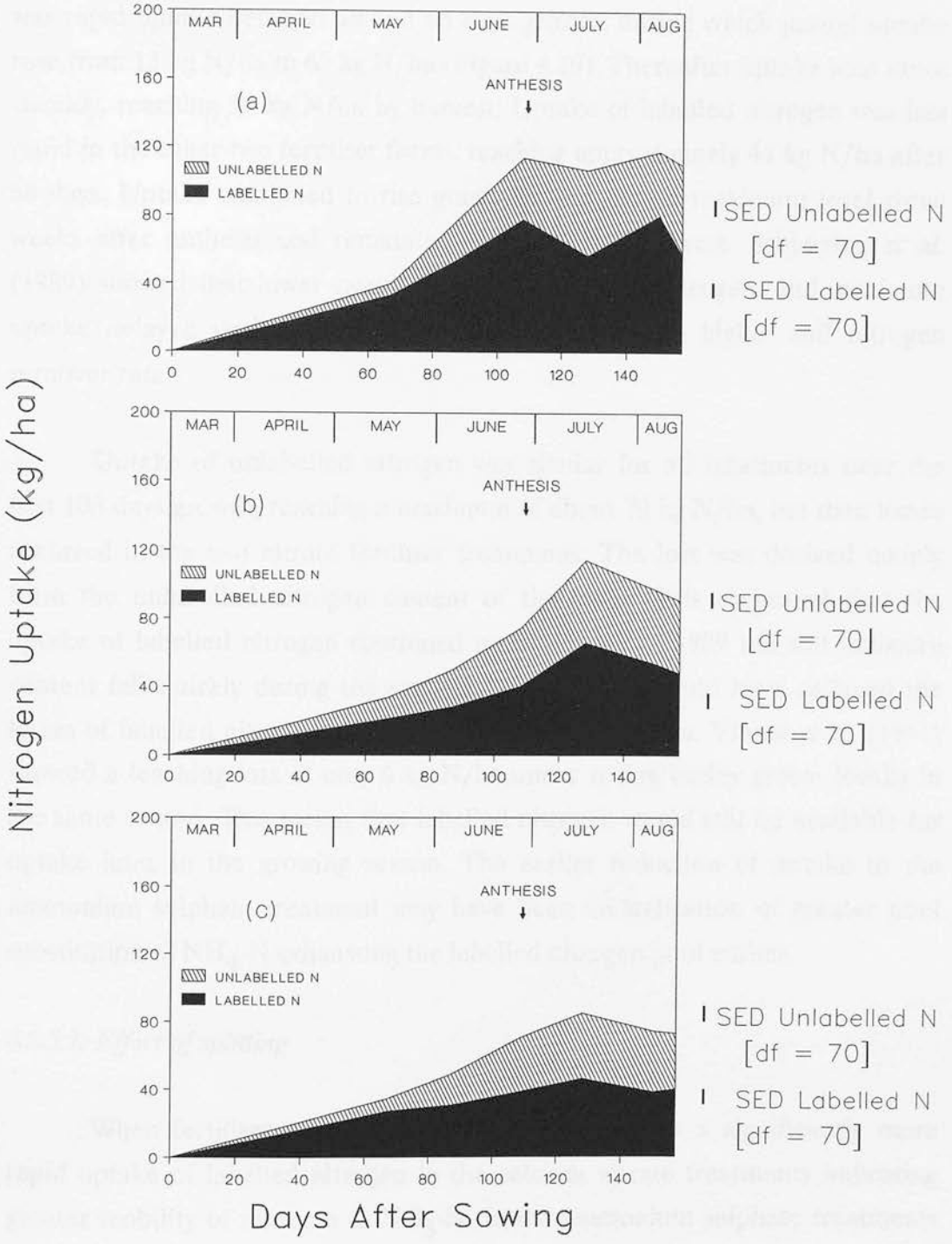


Figure 4.18. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Middlestot 1988

4.5.5: Bush (March Park) 1989

At this site, there was significantly greater uptake of labelled nitrogen applied in the calcium nitrate form. With 120 kg N/ha applied at sowing there was rapid uptake between 48 and 68 days growth, during which period uptake rose from 13 kg N/ha to 63 kg N/ha (Figure 4.19). Thereafter uptake rose more steadily, reaching 98 kg N/ha by harvest. Uptake of labelled nitrogen was less rapid in the other two fertiliser forms, reaching approximately 41 kg N/ha after 68 days. Uptake continued to rise gradually, reaching a maximum level three weeks after anthesis and remaining constant until harvest. Schjørring *et al.* (1989) showed that lower overall uptake of labelled nitrogen, and maximum uptake delayed until after anthesis, was a result of a higher soil nitrogen turnover rate.

Uptake of unlabelled nitrogen was similar for all treatments over the first 108 days growth, reaching a maximum of about 70 kg N/ha, but then losses occurred in the two nitrate fertiliser treatments. The loss was derived mainly from the unlabelled nitrogen content of the plant. This suggested that the uptake of labelled nitrogen continued until harvest. In 1989 the soil moisture content fell quickly during the growing season. This would have reduced the losses of labelled nitrogen via leaching and denitrification. Vinten *et al.* (1991) showed a leaching loss of only 6 kg N/ha under spring barley grown locally in the same season. This means that labelled nitrogen would still be available for uptake later in the growing season. The earlier reduction of uptake in the ammonium sulphate treatment may have been an indication of greater pool substitution of NH_4-N exhausting the labelled nitrogen pool earlier.

4.5.5.1: Effect of splitting

When fertiliser applications were split there was a significantly more rapid uptake of labelled nitrogen in the calcium nitrate treatments indicating greater mobility of nitrogen as NO_3-N. In the ammonium sulphate treatments from 47 to 89 days after sowing, during stem elongation, the uptake of unlabelled nitrogen was greater than labelled nitrogen split applications at 90 kg

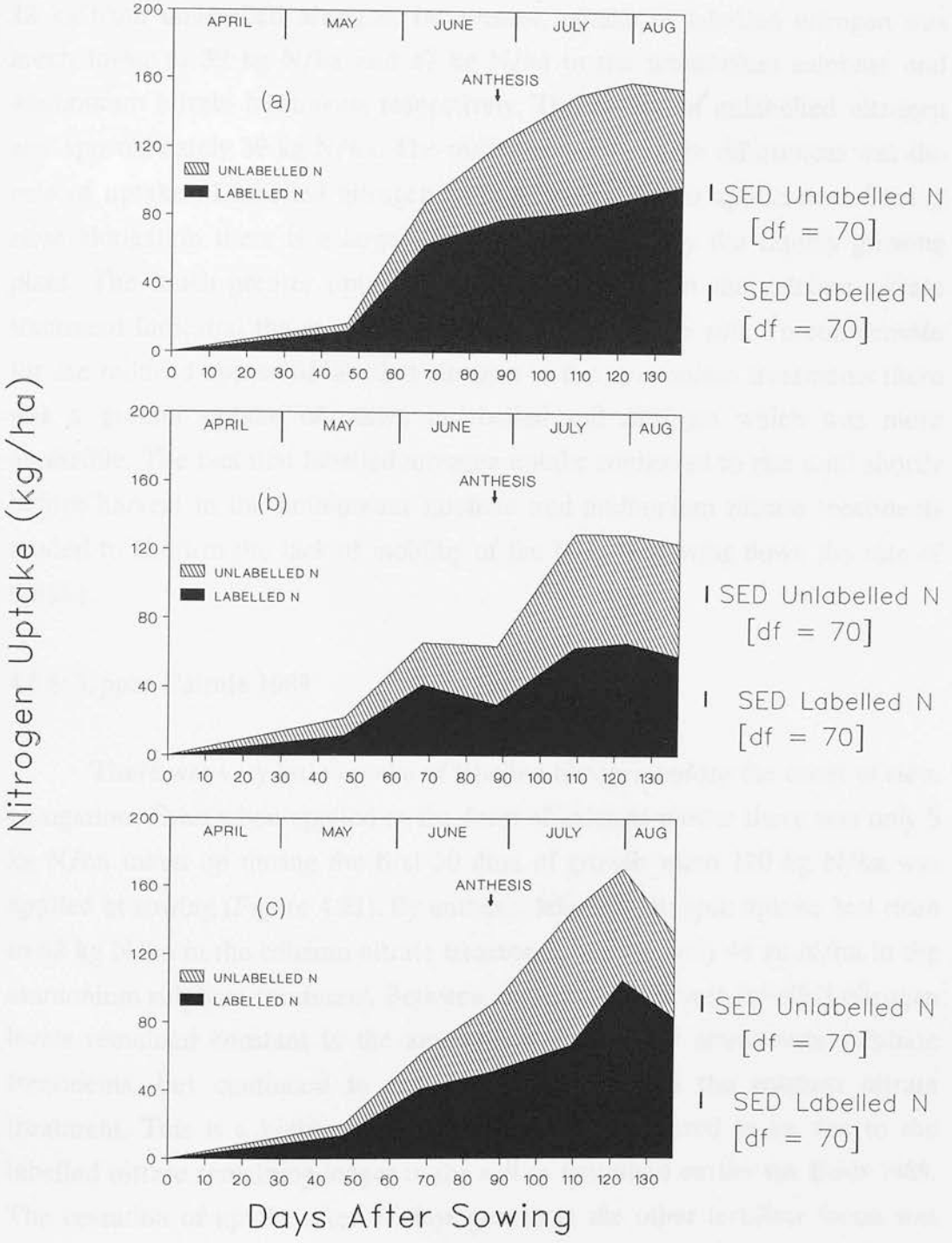


Figure 4.19. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (March Park) 1989

N/ha rates. In the 120 kg N/ha treatment split between sowing and emergence (Figure 4.20) there was a total nitrogen uptake of 81 kg N/ha in the calcium nitrate treatment by the end of the period of stem elongation. Of this 81 kg, 69 kg was derived equally from each of the labelled fertiliser applications, and only 12 kg from unlabelled nitrogen. In contrast, uptake of labelled nitrogen was much lower at 39 kg N/ha and 47 kg N/ha in the ammonium sulphate and ammonium nitrate treatments respectively. The uptake of unlabelled nitrogen was approximately 39 kg N/ha. The main reason for these differences was the rate of uptake of labelled nitrogen from the second split application. During stem elongation there is a large demand for nitrogen by the rapidly growing plant. The much greater uptake of labelled nitrogen in the calcium nitrate treatment indicated the greater mobility of NO_3-N in the soil. To compensate for the reduced uptake of labelled nitrogen in the ammonium treatments there was a greater uptake of native unlabelled soil nitrogen which was more accessible. The fact that labelled nitrogen uptake continued to rise until shortly before harvest in the ammonium sulphate and ammonium nitrate treatments tended to confirm the lack of mobility of the NH_4-N slowing down the rate of uptake.

4.5.6: Upper Cairnie 1989

There was very little uptake of labelled nitrogen before the onset of stem elongation. Even when applied in the form of calcium nitrate there was only 5 kg N/ha taken up during the first 50 days of growth when 120 kg N/ha was applied at sowing (Figure 4.21). By anthesis, labelled nitrogen uptake had risen to 62 kg N/ha in the calcium nitrate treatment, but was only 44 kg N/ha in the ammonium sulphate treatment. Between anthesis and harvest, labelled nitrogen levels remained constant in the ammonium nitrate and ammonium sulphate treatments, but continued to rise by 30 kg N/ha in the calcium nitrate treatment. This is a highly efficient recovery and appeared to be due to the labelled nitrate remaining longer in the soil as described earlier for Bush 1989. The cessation of uptake after 91 days growth in the other fertiliser forms was likely due to the less mobile NH_4-N reducing uptake and also a consequence of pool-substitution shown by the higher uptake of unlabelled nitrogen in the

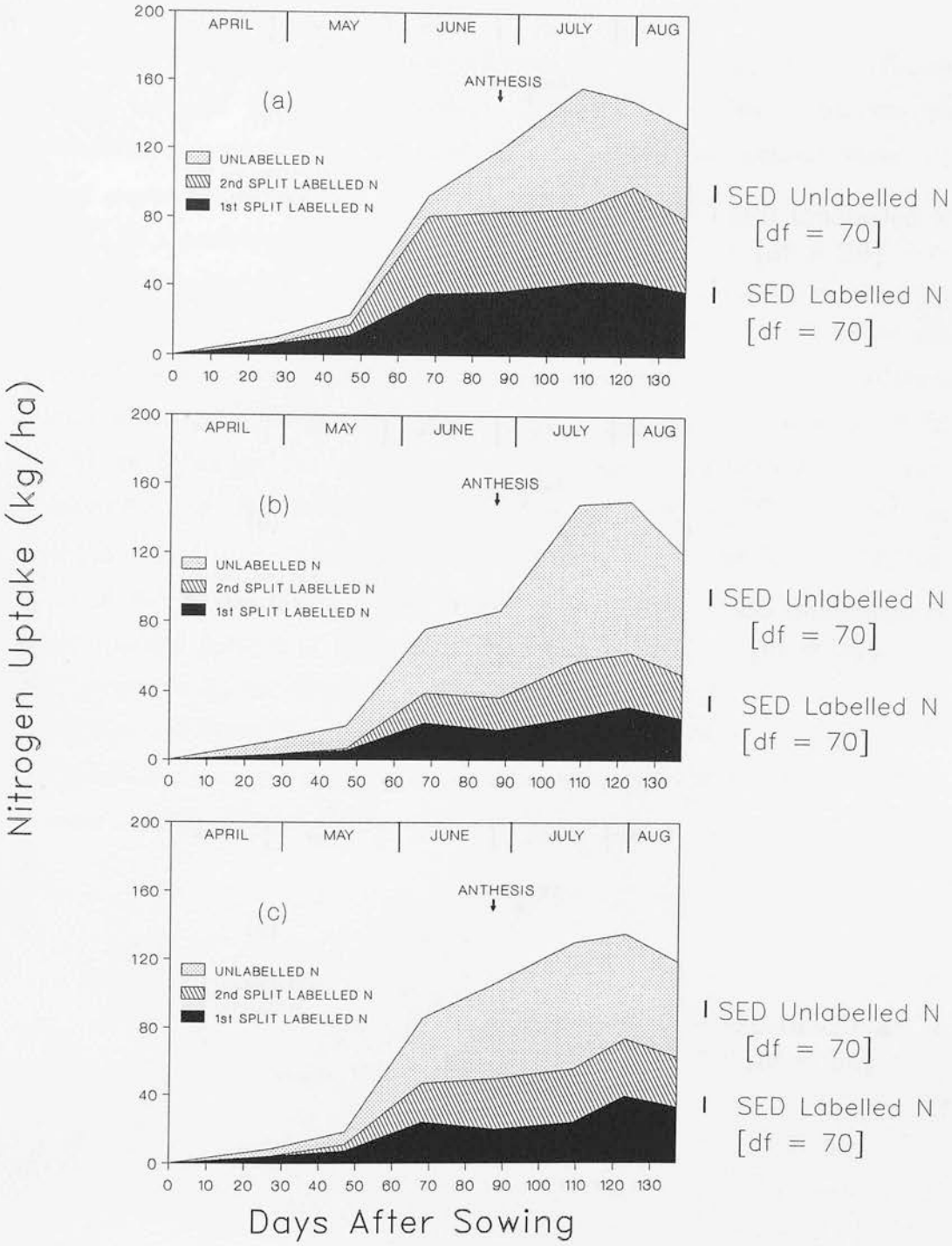


Figure 4.20. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 60 kg/ha at sowing and 60 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (March Park) 1989

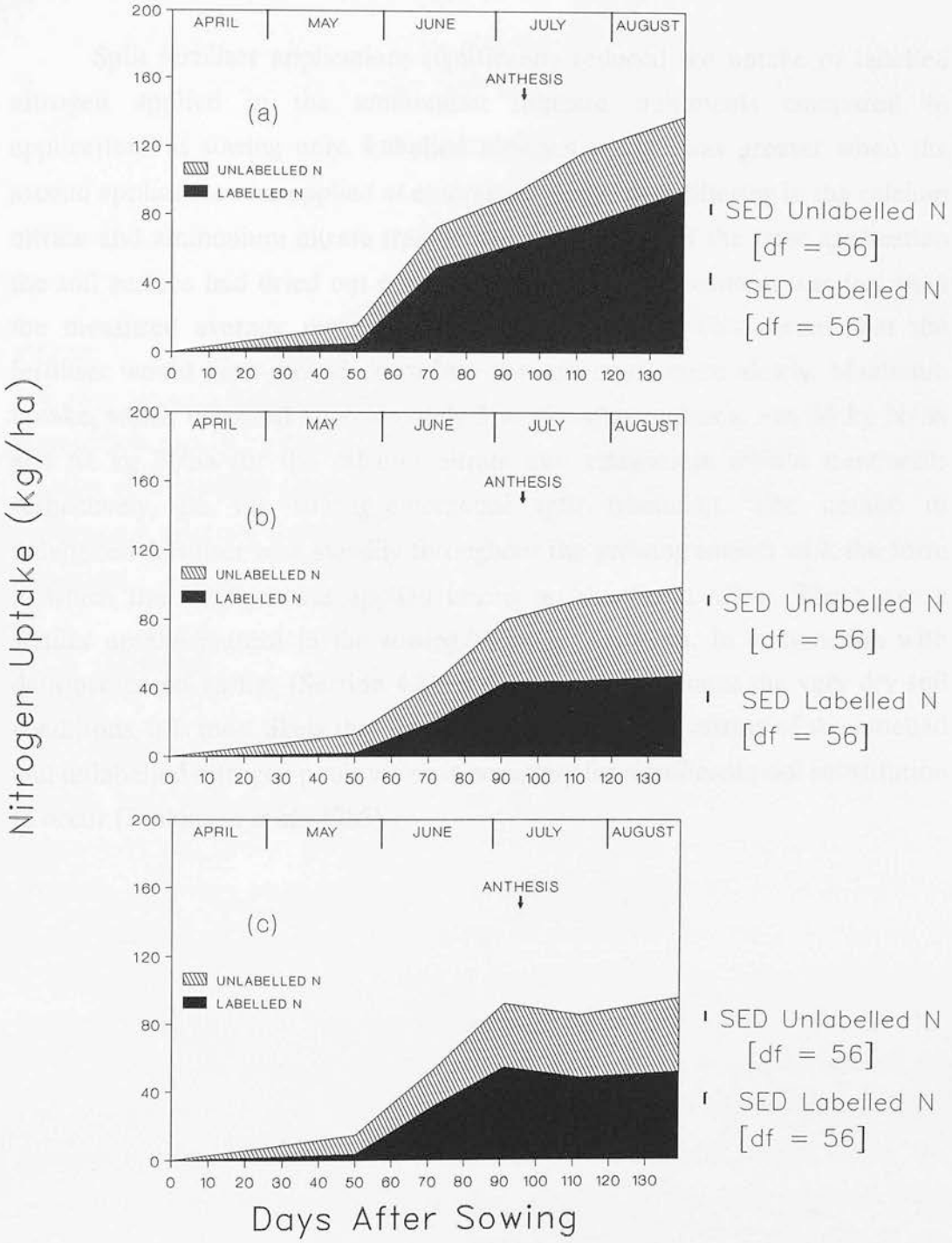


Figure 4.21. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Upper Cairnie 1989

ammonium sulphate treatment. The uptake of unlabelled nitrogen was much lower than at Bush 1989, rising until harvest to 43 kg N/ha in the calcium nitrate and ammonium nitrate treatments and 51 kg N/ha in the ammonium sulphate treatment.

Split fertiliser applications significantly reduced the uptake of labelled nitrogen applied in the ammonium sulphate treatments compared to applications at sowing only. Labelled nitrogen uptake was greater when the second application was applied at emergence rather than tillering in the calcium nitrate and ammonium nitrate treatments. By the time of the later application the soil surface had dried out considerably; its moisture content was less than the measured average moisture content for 0-20 cm. This meant that the fertiliser would have moved down into the soil much more slowly. Maximum uptake, which occurred approximately 3 weeks after anthesis, was 68 kg N/ha and 61 kg N/ha for the calcium nitrate and ammonium nitrate treatments respectively, on the sowing/emergence split treatment. The uptake of unlabelled fertiliser rose steadily throughout the growing season with the form in which the fertiliser was applied having no significant effect. There was a similar uptake pattern in the sowing/tillering treatment. In conjunction with data presented earlier (Section 4.2), and taking into account the very dry soil conditions, it is most likely that there was not a complete mixing of the labelled and unlabelled nitrogen pools which is necessary for significant pool substitution to occur (Jenkinson *et al.*, 1985).

4.6: Uptake of Labelled and Unlabelled Nitrogen in Plant Shoots over the Growing Season, 1990

The uptake of labelled and unlabelled nitrogen from the six sites fertilised with 120 kg N/ha at sowing is discussed. There was no evidence of any losses of labelled nitrogen between anthesis and harvest at any of the sites, although the measurements taken only gave information on any net changes which occurred.

4.6.1: Manorhill

There was no significant further increase in the uptake of labelled nitrogen in the ammonium sulphate treatment after 109 days growth. Between 109 days growth and final harvest, the rate of uptake increased again in the ammonium nitrate treatment, after a lag in uptake over the previous few weeks. Uptake of unlabelled nitrogen remained constant after 109 days growth in the ammonium sulphate treatment, but continued to rise in the ammonium nitrate treatment.

4.6.2: Quixwood

The rate of uptake of labelled nitrogen was low in the early stages of growth, with only 8 kg N/ha taken up by tillering. Uptake was more rapid between 44 and 73 days growth, during stem elongation, reaching 35 kg N/ha by anthesis, and then continuing to rise gradually until harvest in both fertiliser treatments. There was a greater uptake of unlabelled nitrogen compared to labelled nitrogen in the early stages of growth, with uptake rising rapidly after anthesis to 90 kg N/ha. The site at Quixwood was at a higher altitude than the other sites, which reduced the early growth rate and consequently caused the low nitrogen uptake early in the growing season. The high uptake of unlabelled nitrogen appeared to be due to the mineralisation of organic matter in the soil, as illustrated by the increase in mineral nitrogen in the zero fertiliser plots (Section 5.2.2). The organic matter content of the soil was 5.1 % (Table 3.3).

4.6.3: Bush (Crofts and Farmers' Holding)

At the two Bush sites, Crofts and Farmers' Holding, there was more rapid uptake of labelled nitrogen in the ammonium nitrate treatments. At Farmers' Holding a maximum uptake of 51 kg N/ha was achieved in the ammonium nitrate treatment before anthesis then remaining constant until harvest. At Crofts the uptake of labelled nitrogen applied in the same form was greater with uptake levelling off at 64 kg N/ha about two weeks after anthesis. Uptake from the ammonium sulphate-labelled fertiliser rose throughout the season with a final value greater than the ammonium nitrate treatment. After 82 days growth near the end of stem elongation at Crofts, the uptake of unlabelled nitrogen from the ammonium sulphate treatment was higher than the ammonium nitrate treatment, and also greater than labelled nitrogen uptake. However, by harvest there was no significant difference between labelled and unlabelled nitrogen uptake due to continued uptake of labelled nitrogen after anthesis. This indicated the probable occurrence of pool substitution with the late uptake of labelled nitrogen attributed to the re-mineralisation of previously immobilised $^{15}NH_4$-N.

4.6.4: Treaton

There was a rapid uptake of labelled nitrogen between 50 and 83 days growth, during stem elongation, of 45 kg N/ha and 50 kg N/ha for the ammonium sulphate and ammonium nitrate treatments respectively by the end of this period. There was then a loss of around 6 kg N/ha over the next 28 days in both treatments before uptake rose again before harvest to 56 kg N/ha and 60 kg N/ha respectively. Unlabelled nitrogen rose steadily over the first 111 days in both treatments with no significant increase after that.

4.6.5: Kettle

There was very little uptake of nitrogen prior to stem elongation (Figure 4.22b). Between then and anthesis uptake increased rapidly in both treatments by over 50 kg N/ha in 21 days. However, as at Manorhill (Figure 4.22a) and

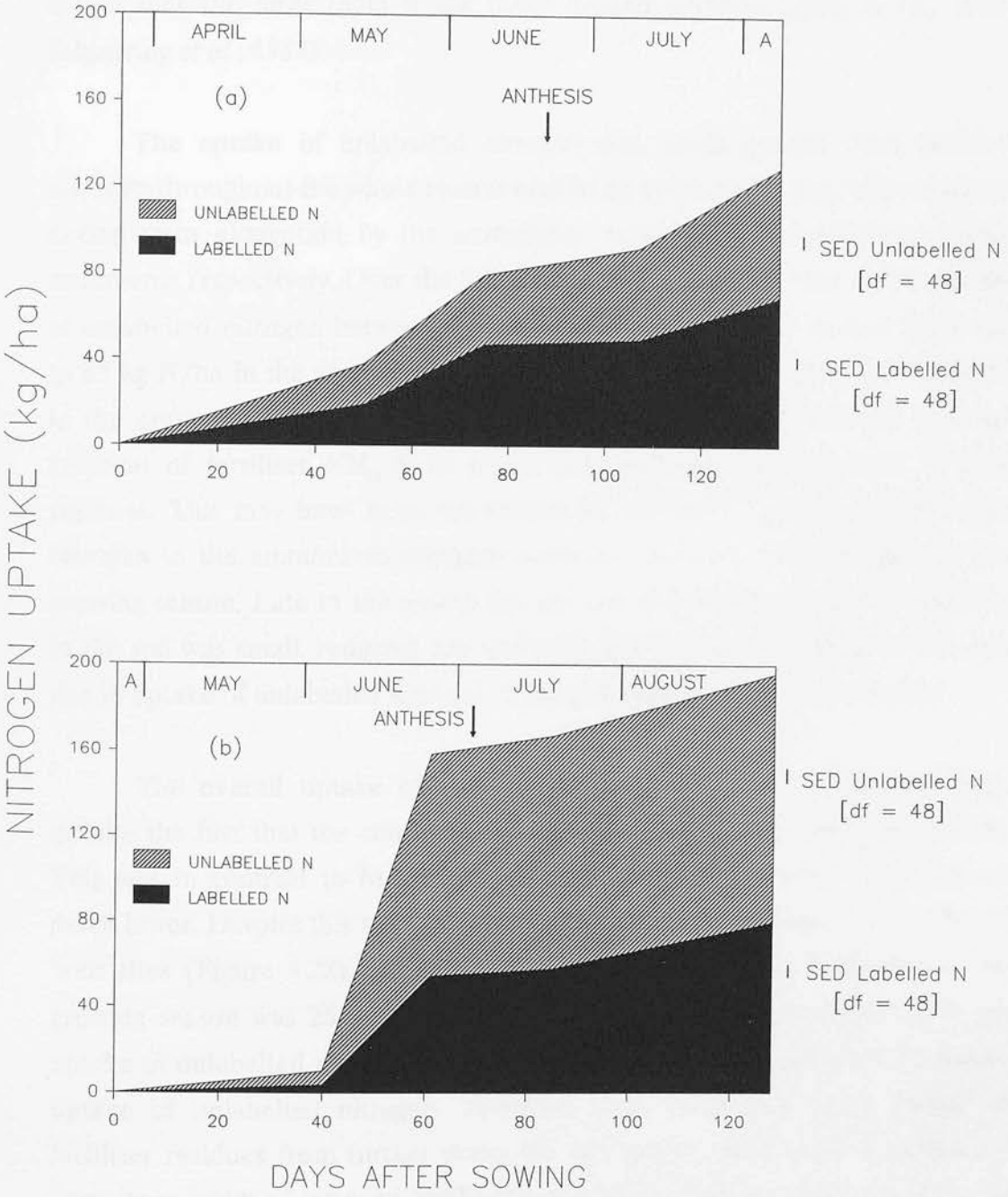


Figure 4.22. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after ammonium nitrate fertiliser applications of 120 kg N/ha at sowing (a) Manorhill 1990 and (b) Kettle 1990

Treaton there was a period of stable or falling labelled nitrogen content over the next 21 days, followed by a rise in uptake once again through to harvest. During this final period of grain filling uptake was greater in the ammonium nitrate treatment. This may have been a reflection of greater losses occurring at the time of anthesis which were reduced later in the season. Other research has shown that the most rapid losses occur around anthesis (Mary *et al.*, 1988; Schjørring *et al.*, 1989).

The uptake of unlabelled nitrogen was much greater than labelled nitrogen throughout the whole season with 85 kg N/ha and 97 kg N/ha taken up during stem elongation by the ammonium sulphate and ammonium nitrate treatments respectively. Over the following 21 days the difference in the uptake of unlabelled nitrogen between the two treatments increased, with a slight fall to 85 kg N/ha in the ammonium sulphate treatment and a rise to 109 kg N/ha in the ammonium nitrate treatment. Clay and Clapp (1990) showed that the addition of fertiliser NH_4-N to a soil inhibited the mineralisation of crop residues. This may have been the reason for the lower uptake of unlabelled nitrogen in the ammonium sulphate treatment during the middle part of the growing season. Late in the season the amount of fertiliser nitrogen remaining in the soil was small, reducing any inhibitory effect and accounting for the late rise in uptake of unlabelled nitrogen in the ammonium sulphate treatment.

The overall uptake of unlabelled nitrogen at Kettle was very high, despite the fact that the concentration of soil organic matter was low (2.8 %). This was in contrast to Manorhill, where uptake of unlabelled nitrogen was much lower. Despite this the uptake of labelled fertiliser nitrogen was similar at both sites (Figure 4.22). At Kettle, residual nitrogen at the beginning of the growing season was 25 kg N/ha, and while this may have contributed to the uptake of unlabelled nitrogen in the plant it was small compared to the overall uptake of unlabelled nitrogen. However, there may have been uptake of fertiliser residues from further down the soil profile, which had accumulated from large inputs of nitrogen fertiliser to vegetable crops in previous seasons, as discussed earlier (Section 4.4). Another source of the unlabelled nitrogen would have been derived from the residues of the previous year's crop (brussels

sprouts). However, Ladd and Amato (1986), using ^{15}N-labelled legume residues, found that these were only partly available to the following crop, with the remainder becoming incorporated into the soil organic matter and were released over a period of years. Azam *et al.* (1989) found that crop residues were mineralised more quickly in soils low in organic matter. This may explain the large uptake of unlabelled nitrogen at Kettle with its light soil texture and low organic matter content.

4.7: General Discussion of Grain Nitrogen Content and Nitrogen Uptake, 1987-1990

The form in which the fertiliser nitrogen was applied had little effect on the nitrogen content in the grain. Where there was an effect, as occurred at Lintlaw and Upper Cairnie the higher grain nitrogen contents in the calcium nitrate treatments were caused by a greater uptake of fertiliser nitrogen compared to the other fertiliser treatments. At low fertiliser rates the calcium nitrate treatments gave higher grain yields than the ammonium sulphate treatments. With increasing fertiliser rates yields reached a maximum at between 90-120 kg N/ha in the calcium nitrate treatments, whereas in the ammonium sulphate treatments yields generally rose steadily with increased fertiliser rates. Sites with dry soil conditions, such as at Middlestot and Upper Cairnie gave higher overall yields in the calcium nitrate treatments compared to the other treatments.

These effects appeared to be determined by the efficiency of recovery of applied fertiliser nitrogen. Calcium nitrate fertiliser was more efficiently recovered in the plant when applied at low rates or in split applications, as this reduced the possibility of losses via leaching or denitrification. The less mobile NH_4-N in the ammonium sulphate treatments reduced recoveries at lower rates as a result of less movement in the soil toward plant roots, and also because of a proportionately greater effect of pool substitution on ^{15}N-labelled fertiliser at low rates (Jenkinson *et al.*, 1985). This effect could have been enhanced by the delayed uptake of fertiliser nitrogen during germination and early growth

immediately after sowing, and also because of the preference of soil microorganisms for NH_4-N as a substrate.

Split applications only increased yields over those resulting from seedbed applied fertiliser in the calcium nitrate treatments applied to the early sown crop at Lintlaw. Heavy rain shortly after sowing reduced the uptake of calcium nitrate all applied at sowing probably due to increased leaching. Grain nitrogen concentrations were generally not significantly affected by split applications. In 1989 split applications at the lower rate of 90 kg N/ha gave lower grain nitrogen contents when compared with 120 kg N/ha all applied at sowing, but did not significantly reduce yields. This year, however, soil conditions were very dry and this led to very high grain nitrogen contents. This appeared to be caused by a reduction in the grain filling period due to moisture stress in the plant and this reduced the amount of photosynthate translocated to the grain. In 1990 there was no significant difference in grain yields and grain nitrogen concentrations between the ammonium sulphate and ammonium nitrate treatments studied at 120 kg N/ha.

The uptake of labelled nitrogen occurred mainly during the early part of the growing season. After an initial period of low uptake, there was generally a dramatic rise in uptake as the plant entered the period of stem elongation, most notably in the calcium nitrate and ammonium nitrate treatments, and reached a maximum around anthesis. Losses of labelled nitrogen between anthesis and harvest were recorded at some sites. These were most significant in the calcium nitrate and ammonium nitrate treatments at sites where there was a large and rapid uptake of labelled nitrogen, such as occurred at Bush 1988, where losses of up to 25 kg N/ha were recorded. The concentration of nitrogen in these plant tissues would have been high, and this seemed to determine the extent of nitrogen losses. Reports of losses of fertiliser nitrogen from plant tissues have been reported and it has been suggested that these losses could have occurred as a result of root exudation (Cooper *et al.*, 1986; Recous *et al.*, 1988b; Janzen, 1990), or ammonia volatilisation from senescing plant tissues later in the growing season (Harper *et al.*, 1987; Schjørring *et al.*, 1989).

When applied in the form of ammonium sulphate, the uptake of labelled nitrogen was slower, continuing later into growing season than the other fertiliser forms. This may have been due to the less mobile NH_4-N restricting root uptake early in the growing season, but also remaining longer in the soil. Another possible reason for the late uptake of labelled nitrogen could have been the re-mineralisation of previously immobilised $^{15}NH_4$-N later in the growing season.

Similar patterns of uptake of labelled nitrogen were recorded under very dry conditions at Middlestot and Upper Cairnie in the calcium nitrate and ammonium nitrate treatments. Uptake of labelled nitrogen continued late into the growing season at these two sites, up to harvest at Upper Cairnie, due to the reduced mobility of NO_3-N in the soil under these conditions. There were no losses of labelled nitrogen from the plants at these sites which could have been attributed to the lower accumulation of nitrogen in the plant tissues around the time of anthesis compared to results from the other sites.

The uptake of unlabelled nitrogen was not as rapid as labelled nitrogen especially through the rapid uptake phase during stem elongation. Over this period the uptake of unlabelled nitrogen was higher in the ammonium sulphate treatments compared with the other fertiliser forms. This was probably due to a combination of pool substitution of NH_4-N, and also the uptake of unlabelled NO_3-N when the plant was unable to satisfy its high demand for nitrogen from the less mobile applied $^{15}NH_4$-N. Uptake of unlabelled nitrogen continued after labelled nitrogen uptake had ceased, continuing to rise until harvest under the dry soil conditions at Middlestot and Upper Cairnie while remaining constant from shortly after anthesis at the other sites. This constant uptake occurred despite the significant losses of labelled nitrogen from the plant which suggested that there would also have been some losses of unlabelled nitrogen given no discrimination between ^{15}N and ^{14}N. This meant that there would also have been continued uptake of unlabelled nitrogen until harvest at these sites, indicating continued mineralisation of soil organic matter, as by this time mineral nitrogen levels in the soil were low at most sites. At Upper Cairnie the crop residues from the previous season were oil seed rape, which could have

resulted in greater net mineralisation than from cereal residues as the soil temperature increased during the growing season.

However, these treatments studying the effect of fertiliser form and timing on grain nitrogen concentrations and yields were found to be relatively small when compared to the effects of site and season. The most important determining factor at each site was the uptake of unlabelled nitrogen in the plant. Uptake of unlabelled nitrogen was significantly more variable between sites than the uptake of labelled nitrogen. Variation in the uptake of unlabelled soil nitrogen between sites ranged up to 100 % even between sites of similar cropping histories grown in the same season. Most of these sites would have been categorised as N-Index zero soils, based on previous cropping (MAFF, 1985), which would have meant similar fertiliser recommendations. Therefore it appeared that the most important factor to be determined, to assist in the production of a good crop of malting barley, was an assessment of the likely uptake of soil nitrogen in the crop. Results of assessments made using simple laboratory techniques are presented in Section 7.

5: MINERAL NITROGEN IN THE SOIL, 1987-1990

In this section the effect of site and treatment differences on the quantity of mineral nitrogen in the upper soil profile during the growing season is discussed. Representative diagrams are presented in the main text, with the remaining diagrams to be found in the appendix.

5.1: 1987-1989 Seasons

5.1.1: Bush (Seafield) 1987

At this site, the amount of mineral nitrogen in the soil declined steadily over the first 82 days growth after the addition of 120 kg N/ha ammonium nitrate in the seedbed (Figure 5.1a). Thereafter there was no significant change in the amount of mineral nitrogen in the soil. Over the initial 82 days there was a reduction of 108 kg/ha mineral nitrogen, which was of the same order as total nitrogen uptake in the plant tissues (Section 4.5.1). The lack of any significant decline in mineral nitrogen after this, despite the continued uptake of unlabelled nitrogen in the plants, suggested that net mineralisation continued up until harvest.

5.1.2: Lintlaw 1987

Here, the rate of decline of mineral nitrogen in the soil, over the first 54 days growth, was similar for both 120 kg N/ha and 150 kg N/ha treatments (Figure 5.1b). By this time there was an even distribution of mineral nitrogen in the top 40 cm of the soil in the 120 kg N/ha treatment (Figure 5.2b). This mineral nitrogen contained only 24 kg NH_4-N/ha indicating a greater rate of nitrification, and was significantly lower as a proportion of the total mineral nitrogen than the NH_4-N present in the soil at Bush. This was probably a consequence of the lighter soil texture at Lintlaw (Table 3.1) allowing more solute movement, and possibly better aeration increasing nitrification activity. There then followed a more rapid decline over the following 14 days, which was greater in the 150 kg N/ha treatment. By 100 days' growth, the decline in soil mineral nitrogen ceased, with no further change up to harvest. During this later

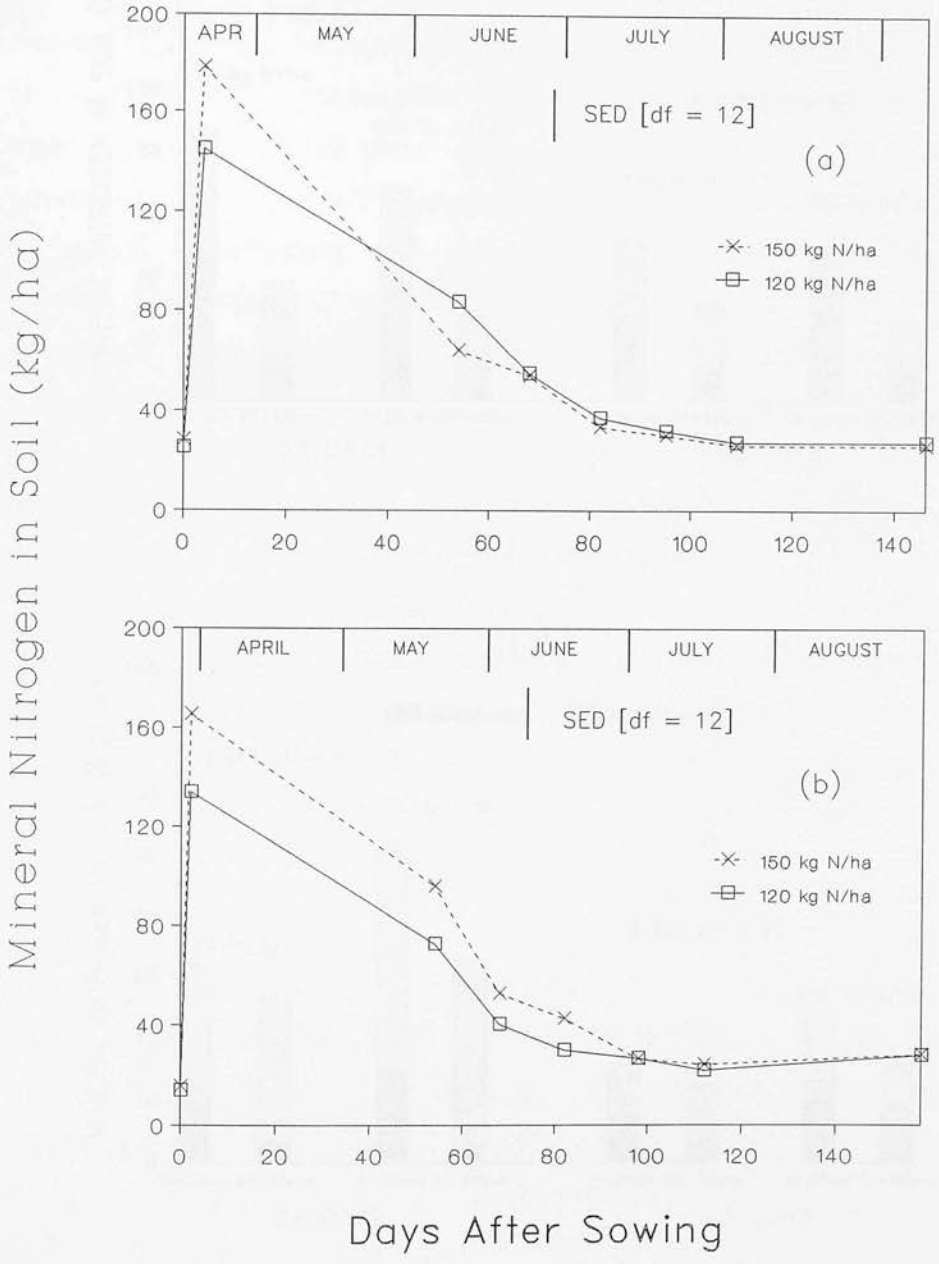


Figure 5.1. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley applied with ammonium nitrate fertiliser at sowing, (a) Bush (Seafield) and (b) Lintlaw, 1987

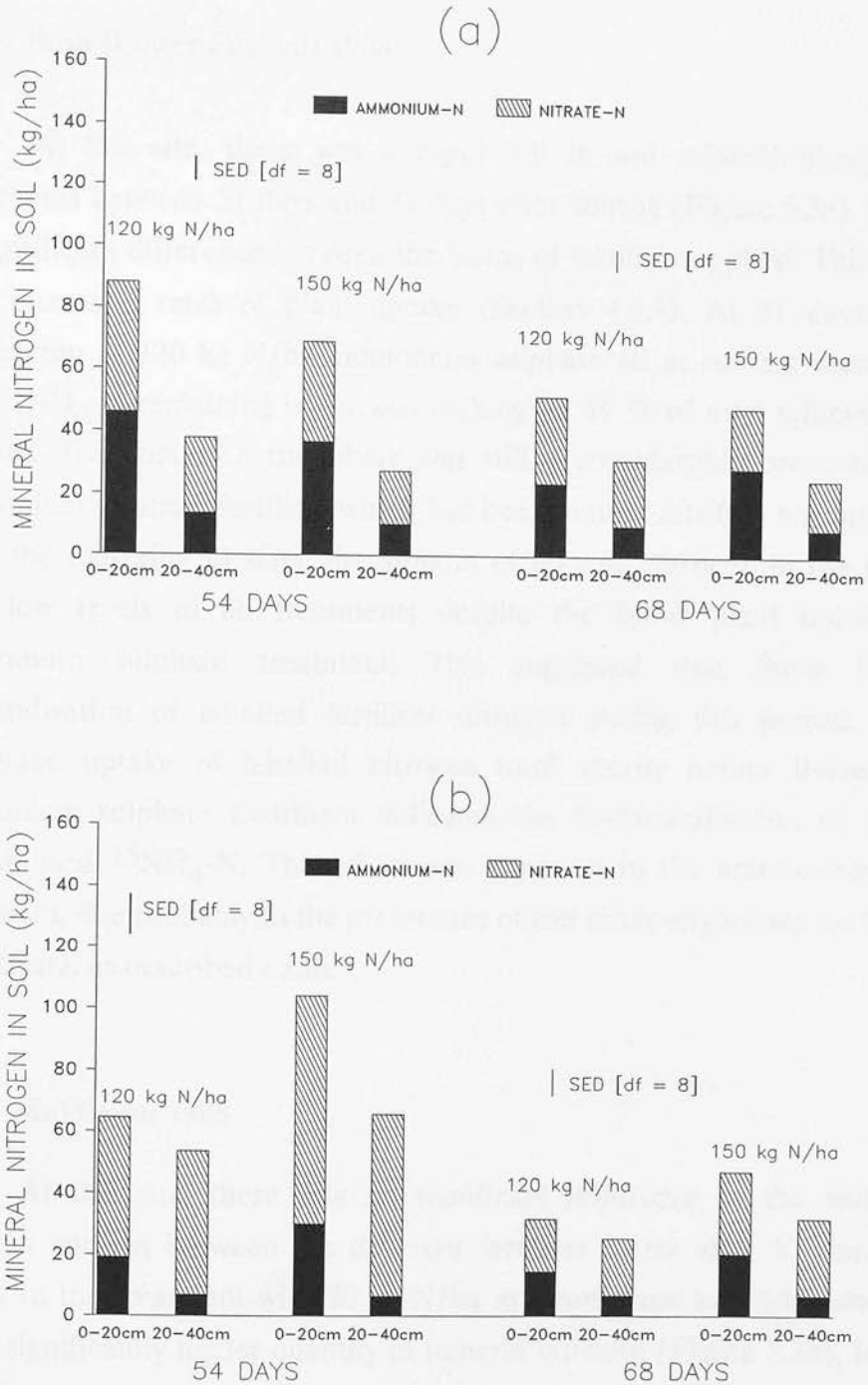


Figure 5.2. Quantities of nitrate- and ammonium-N at different depths in the soil at first two sampling dates, under spring barley fertilised with ammonium nitrate at sowing, (a) Bush (Seafield) and (b) Lintlaw, 1987

growth period there was continued uptake of unlabelled nitrogen in the plant. This suggested that mineralisation proceeded through until harvest.

5.1.3: Bush (Lower Fulford) 1988

At this site, there was a rapid fall in soil mineral nitrogen in all treatments between 51 days and 72 days after sowing (Figure 5.3a). There was no significant difference between the forms of fertiliser applied. This coincided with increased rates of plant uptake (Section 4.5.3). At 51 days after the application of 120 kg N/ha ammonium sulphate all at sowing, there were 49 kg/ha NH_4-N remaining in the soil making up 49 % of total mineral nitrogen present. This indicated that there was still a considerable proportion of the ammonium sulphate fertiliser which had been neither nitrified nor immobilised. Over the following 21 days, the amount of mineral nitrogen in the soil fell to very low levels in all treatments despite the lower plant uptake in the ammonium sulphate treatment. This suggested that there had been immobilisation of labelled fertiliser nitrogen during this period. Also the continued uptake of labelled nitrogen until shortly before harvest in the ammonium sulphate treatment indicated the re-mineralisation of previously immobilised $^{15}NH_4$-N. This effect was apparent in the ammonium sulphate treatment, due probably to the preference of soil micro-organisms for NH_4-N as a substrate, as described earlier.

5.1.4: Middlestot 1988

At this site, there was no significant difference in the soil mineral nitrogen content between the different fertiliser forms after 67 days growth, except in the treatment with 90 kg N/ha as ammonium sulphate, where there was a significantly higher quantity of mineral nitrogen (Figure 5.3b). In the 120 kg N/ha treatments there was significantly more nitrogen in the top 0-20 cm of the soil than 20-40 cm in the two treatments with ammonium-containing fertiliser (Figure 5.4). This indicated that the applied NH_4-N was less mobile than the NO_3-N applied in the calcium nitrate treatment, and therefore was not

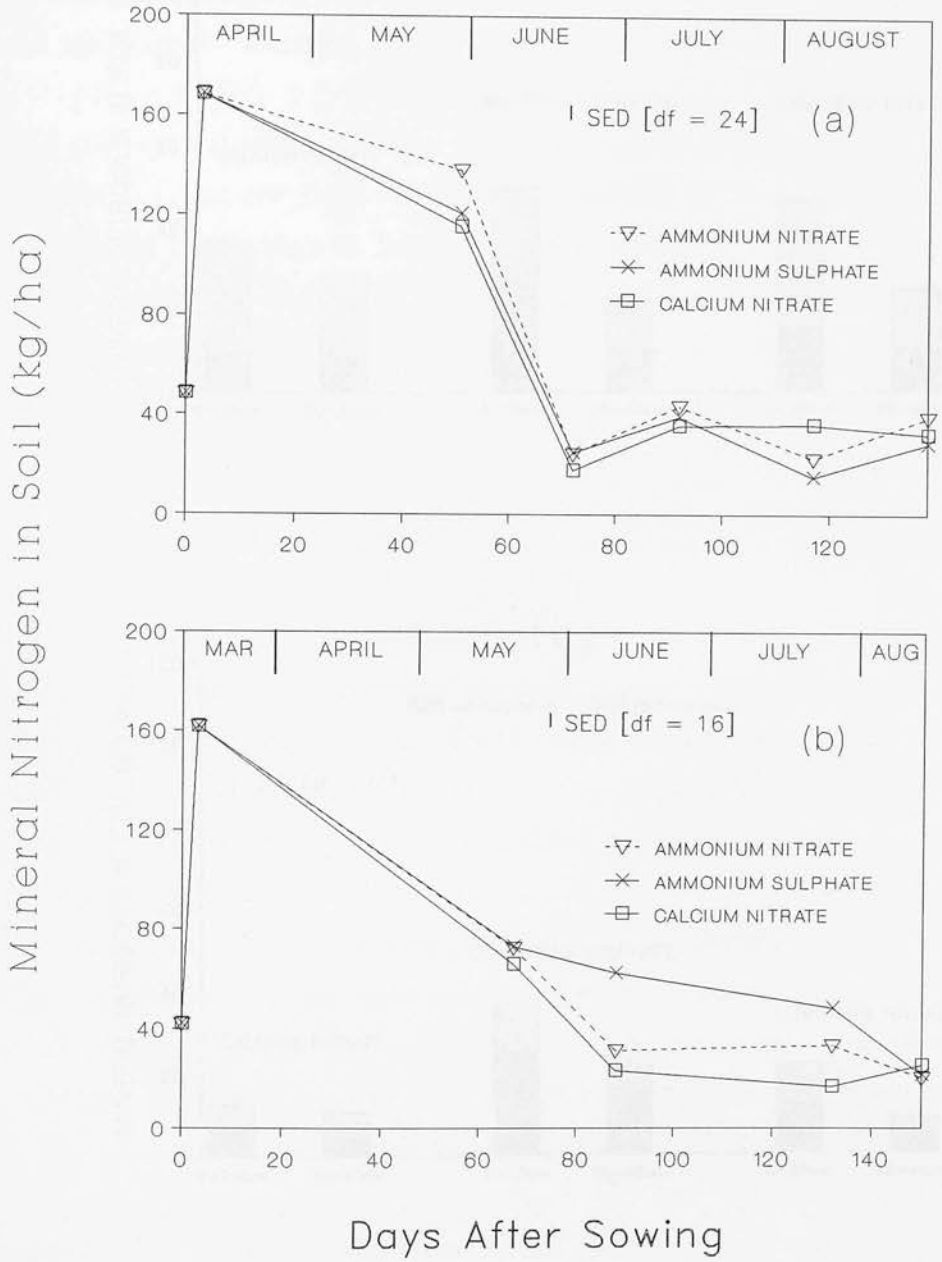


Figure 5.3. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley, with 120 kg/ha fertiliser nitrogen applied at sowing (a) Bush (Lower Fulford) 1988 and (b) Middlestot 1988

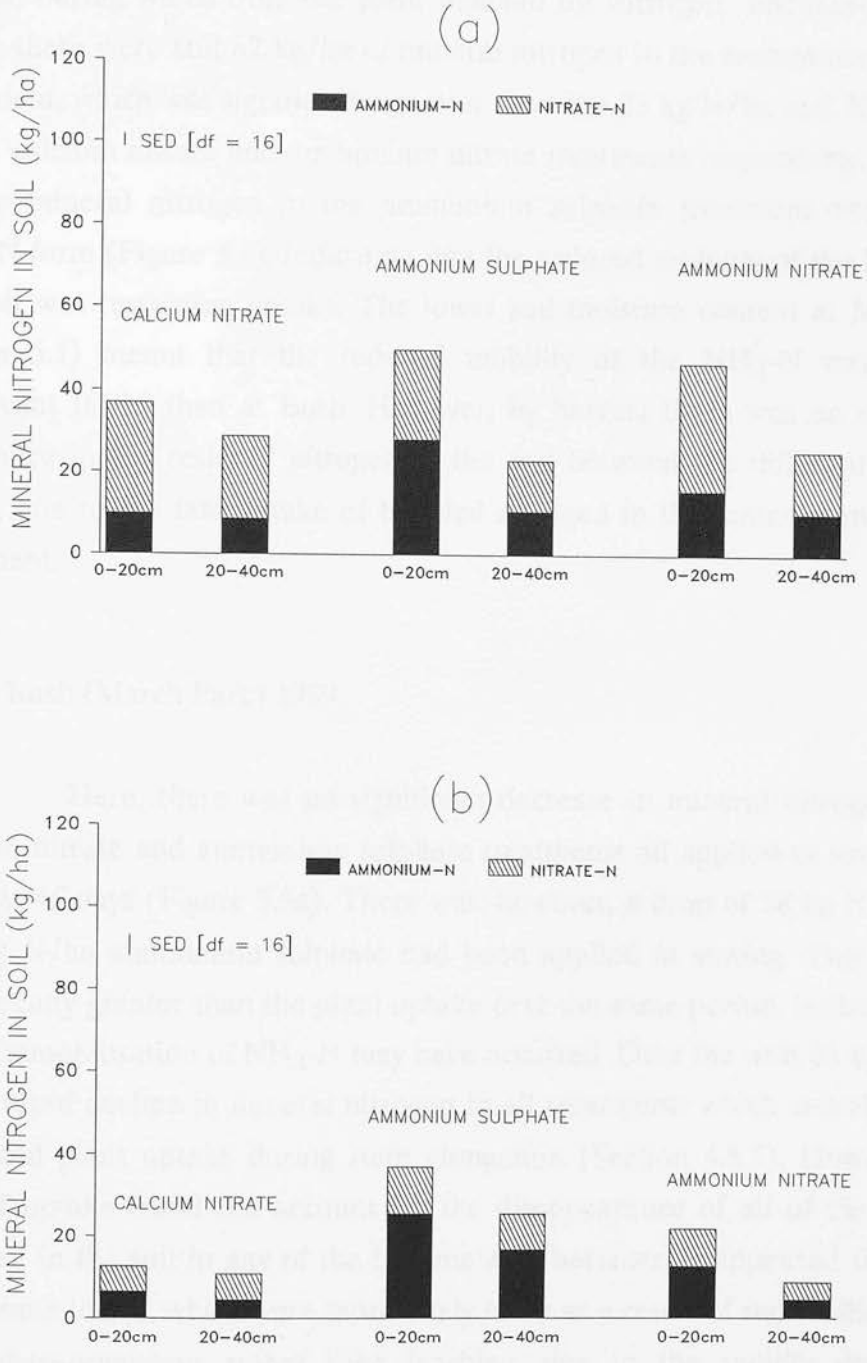


Figure 5.4. Quantities of nitrate- and ammonium-N at different depths in the soil at first two sampling dates, under spring barley fertilised with 120 kg/ha N fertiliser at sowing, (a) after 67 days (b) after 88 days, Middlestot 1988

so well distributed throughout the soil profile, reducing its availability to roots other than those growing close to the soil surface. After a further 21 days growth, during which time the plant demand for nitrogen increased (Section 4.5.4), there were still 62 kg/ha of mineral nitrogen in the ammonium sulphate treatment, which was significantly greater than the 23 kg N/ha and 32 kg N/ha in the calcium nitrate and ammonium nitrate treatments respectively. 42 kg/ha of the mineral nitrogen in the ammonium sulphate treatment were in the NH_4-N form (Figure 5.4), indicating that the reduced mobility of the NH_4-N in the soil was restricting uptake. The lower soil moisture content at Middlestot (Table 5.1) meant that the reduced mobility of the NH_4-N was a more significant factor than at Bush. However, by harvest there was no significant difference in the residual nitrogen in the soil between the different fertiliser forms, due to the late uptake of labelled nitrogen in the ammonium sulphate treatment.

5.1.5: Bush (March Park) 1989

Here, there was no significant decrease in mineral nitrogen in the calcium nitrate and ammonium sulphate treatments all applied at sowing over the first 45 days (Figure 5.5a). There was, however, a drop of 38 kg N/ha after 120 kg N/ha ammonium sulphate had been applied at sowing. This loss was significantly greater than the plant uptake over the same period, indicating that some immobilisation of NH_4-N may have occurred. Over the next 21 days there was a rapid decline in mineral nitrogen in all treatments which coincided with increased plant uptake during stem elongation (Section 4.5.5). However, the rate of uptake could not account for the disappearance of all of the mineral nitrogen in the soil in any of the treatments. Therefore, it appeared that there were some losses, which were more likely to be as a result of immobilisation by soil micro-organisms rather than leaching, due to the rapidly drying soil conditions (Table 5.2) and the imperfectly draining soil texture (Table 3.1). In both the ammonium sulphate and ammonium nitrate treatments there was significantly less movement of mineral nitrogen down the soil profile over the first 45 days growth, compared with the calcium nitrate treatment, and this was

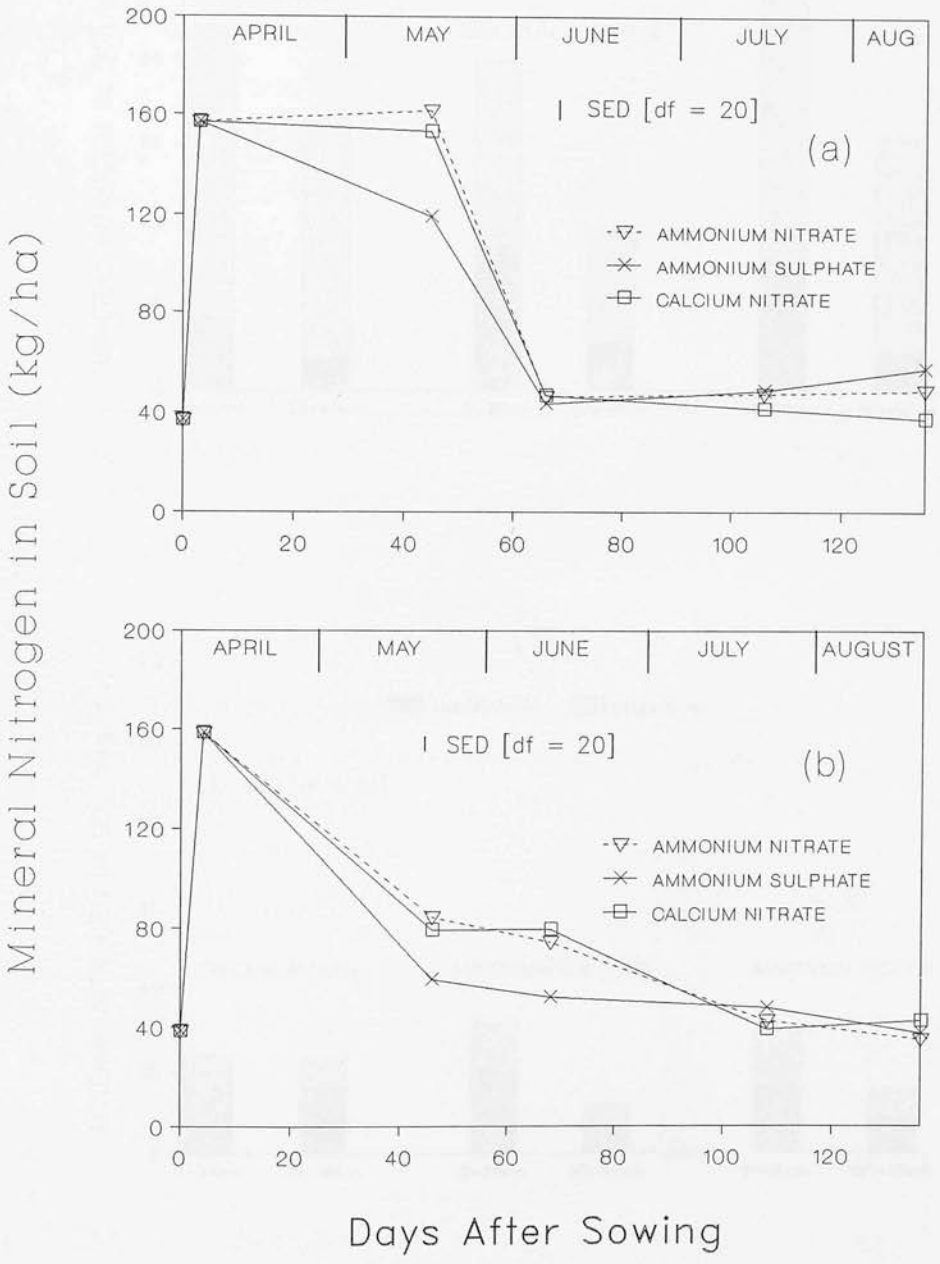


Figure 5.5. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley, with 120 kg/ha fertiliser nitrogen applied at sowing (a) Bush (March Park) 1989 and (b) Upper Cairnie 1989

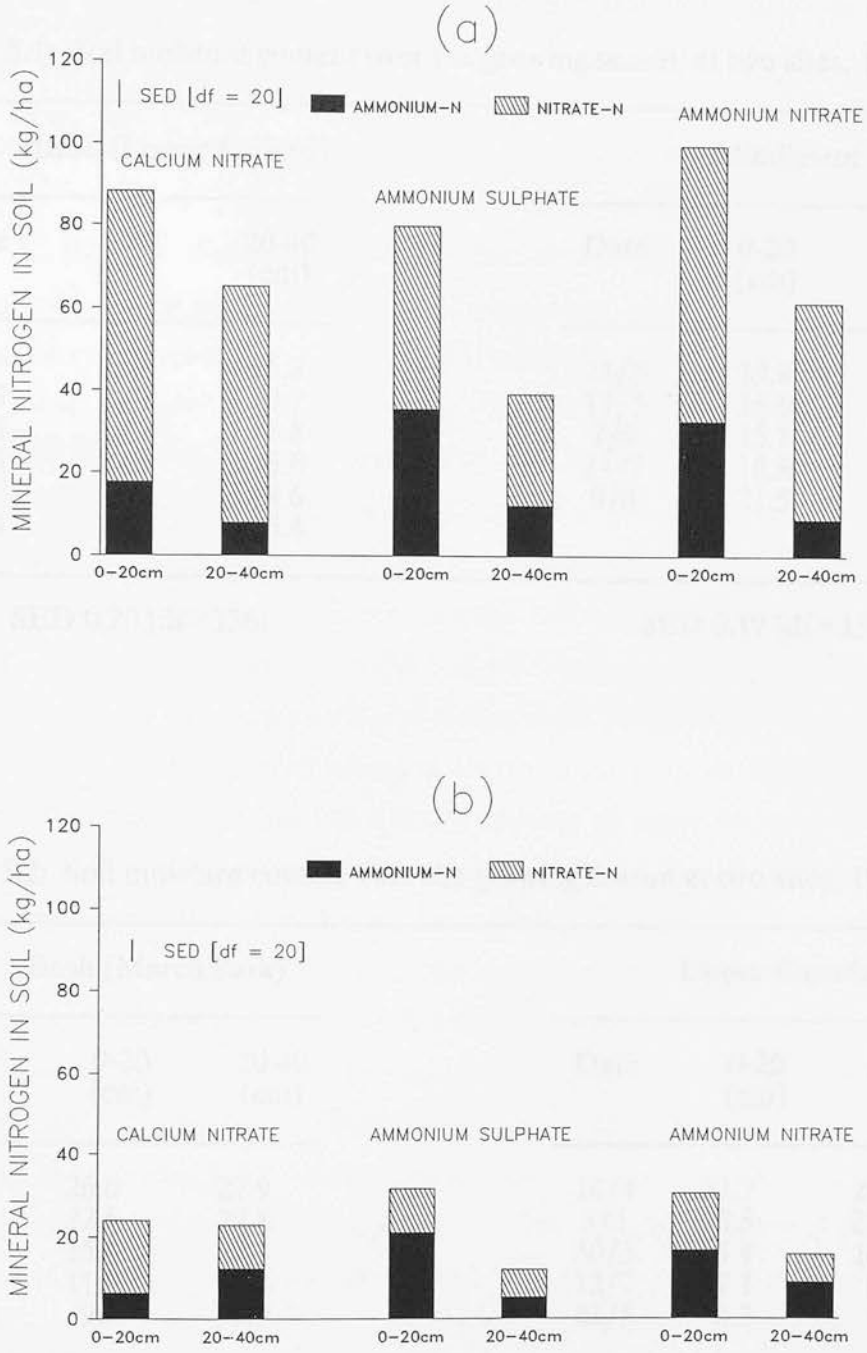


Figure 5.6. Quantities of nitrate- and ammonium-N at different depths in the soil at first two sampling dates, under spring barley fertilised with 120 kg/ha N fertiliser at sowing, (a) after 45 days (b) after 66 days, Bush (March Park) 1989

Table 5.1: Soil moisture content over the growing season at two sites, 1988

Bush (Lower Fulford)			Middlestot		
Date	0-20 (cm)	20-40 (cm)	Date	0-20 (cm)	20-40 (cm)
5/4	21.6	25.3	11/3	15.8	19.8
25/5	22.7	23.7	17/5	15.6	15.9
11/6	13.8	15.8	7/6	15.1	16.0
19/6	22.9	15.6	21/7	16.8	15.8
4/7	24.9	24.6	9/8	21.5	20.9
20/8	24.6	25.4			
SED 0.20 [df = 136]			SED 0.19 [df = 136]		

Table 5.2: Soil moisture content over the growing season at two sites, 1989

Bush (March Park)			Upper Cairnie		
Date	0-20 (cm)	20-40 (cm)	Date	0-20 (cm)	20-40 (cm)
13/4	26.6	27.9	14/4	22.7	24.6
4/5	22.5	24.8	5/5	18.5	21.4
31/5	15.4	16.3	30/5	15.4	16.8
13/7	11.0	11.7	12/7	7.1	8.4
16/8	9.8	9.9	22/8	8.3	9.0
SED 0.17 [df = 136]			SED 0.85 [df = 136]		

still apparent after 66 days (Figure 5.6). At this time, after 66 days, there were still over 43 kg/ha of mineral nitrogen in the soil in all treatments. This might explain the continued uptake of labelled nitrogen late in the growing season as described on Section 4.5.5.

5.1.6: Upper Cairnie 1989

At this site, there was a steady decline in soil mineral nitrogen from sowing until shortly before harvest in all treatments, which did not appear to be influenced by increased rates of plant uptake after 48 days growth (Figure 5.5b). There were greater losses of mineral nitrogen in the ammonium sulphate treatments over the first 48 days compared with the calcium nitrate and ammonium nitrate treatments; up to 20 kg N/ha greater in the 120 kg N/ha treatments. This difference could not be accounted for by plant uptake and therefore possibly indicated greater immobilisation of NH_4-N by soil microbes. At this time there were only 28 kg/ha NH_4-N remaining in the soil out of 120 kg N/ha ammonium sulphate applied at sowing with 31 kg/ha present as NO_3-N. Total labelled and unlabelled nitrogen uptake in the plant at this time was only 13 kg/ha, so therefore there was a disappearance of approximately 45 kg N/ha from the soil mineral nitrogen pool. In the calcium nitrate and ammonium nitrate treatments the unaccounted for mineral nitrogen was less, with more mineral nitrogen retained in the soil. The amount of mineral nitrogen in the soil remained high with 80 kg/ha present, even after 68 days growth, in the calcium nitrate and ammonium nitrate treatments. It appeared that the rapidly drying soil conditions (Table 5.2) and heavier soil texture at Upper Cairnie (Table 3.1) reduced the possibility of leaching, and also reduced the movement of soil nutrients towards plant roots. This could explain the steady uptake of labelled nitrogen with calcium nitrate up to harvest.

5.2: 1990 Season

The quantities of mineral nitrogen in the soil at the six sites studied in 1990 are discussed in this section.

5.2.1: Manorhill

Here, the quantity of mineral nitrogen in the ammonium sulphate treatment fell steadily over the first 50 days growth, from 151 kg N/ha to 75 kg N/ha (Figure 5.7a). In contrast, the decline in the ammonium nitrate treatment was smaller, falling to 102 kg N/ha after 50 days. This was despite a similar rate of uptake in the plant (Section 4.6.1), suggesting that there may have been greater immobilisation of NH_4-N in the ammonium sulphate treatment. Over the following 25 days, the quantity of mineral nitrogen in the soil fell to 25 kg N/ha in the ammonium sulphate treatment and 13 kg N/ha in the ammonium nitrate treatment. The greater quantity of mineral nitrogen in the ammonium sulphate treatment appeared to be due to a greater amount of NH_4-N retained in the soil (Figure 5.8) during a period of increased plant uptake. This could have been the result of reduced NH_4-N mobility in the dry soil conditions (Table 5.3).

5.2.2: Quixwood

At this site, there was a significant rate of net mineralisation in the zero fertiliser treatment over the first 44 days as illustrated by the increase in mineral nitrogen. Over this initial growth period uptake of labelled nitrogen in the fertilised plots was low, but despite this there was a large decline in soil mineral nitrogen in the fertilised plots. This decline, therefore, appeared to be due to the immobilisation of labelled fertiliser nitrogen. These two factors, and the high soil organic matter levels (Table 3.3), indicated that there was significant mineralisation/immobilisation turnover of nitrogen in the soil. Also, the form in which the mineral nitrogen was present in the soil after 44 days (Figure 5.8) showed that the mineralised nitrogen in the zero plots was nitrified very rapidly. At this time there were only 33 kg/ha and 21 kg/ha of NH_4-N in the mineral nitrogen pools of the ammonium sulphate and ammonium nitrate treatments

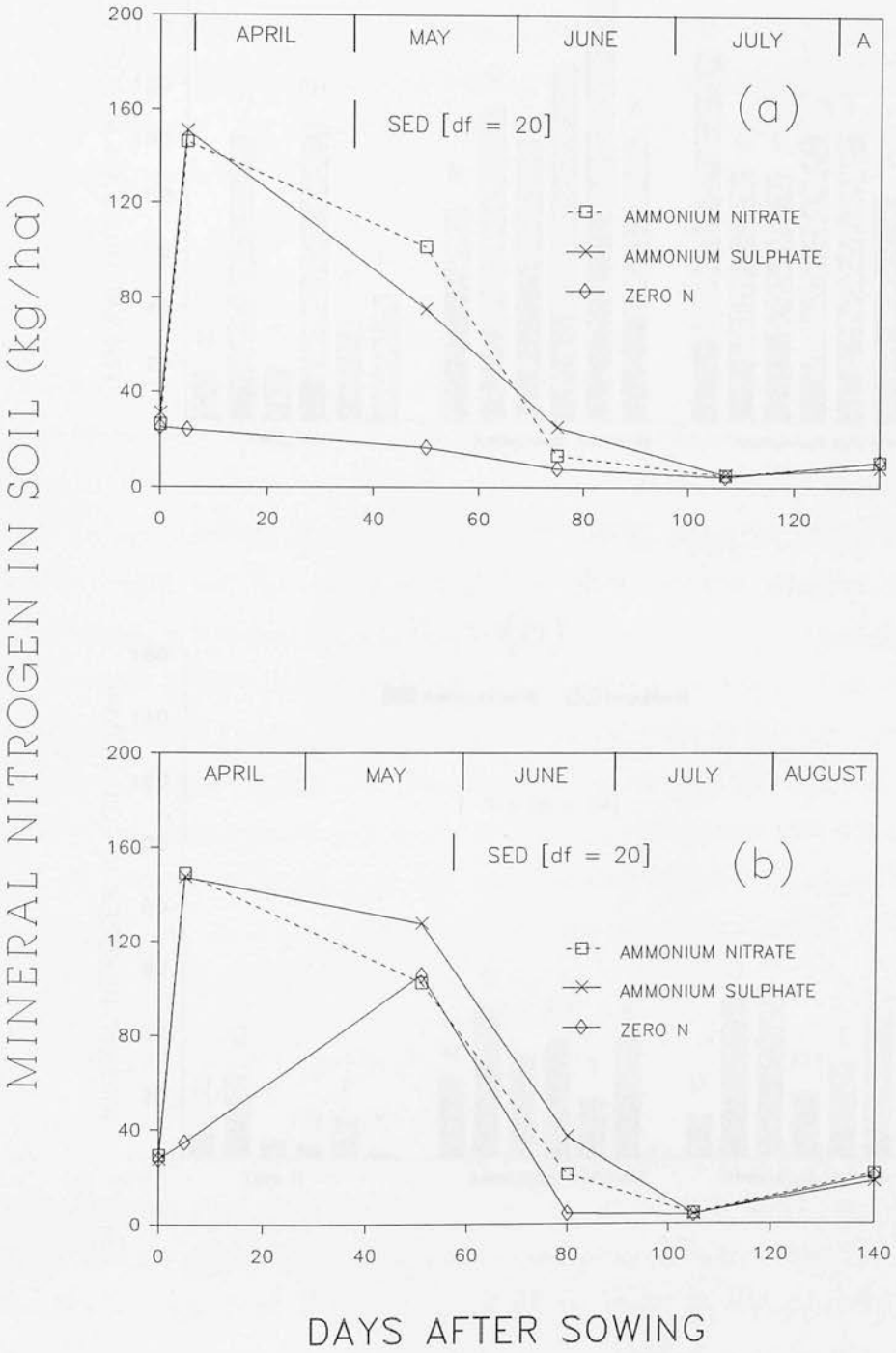


Figure 5.7. Changes in mineral nitrogen in the soil (0-30 cm) over the growing season, under spring barley, with 120 kg/ha fertiliser nitrogen applied at sowing (a) Manorhill 1990 (b) Bush (Fm. Holding) 1990

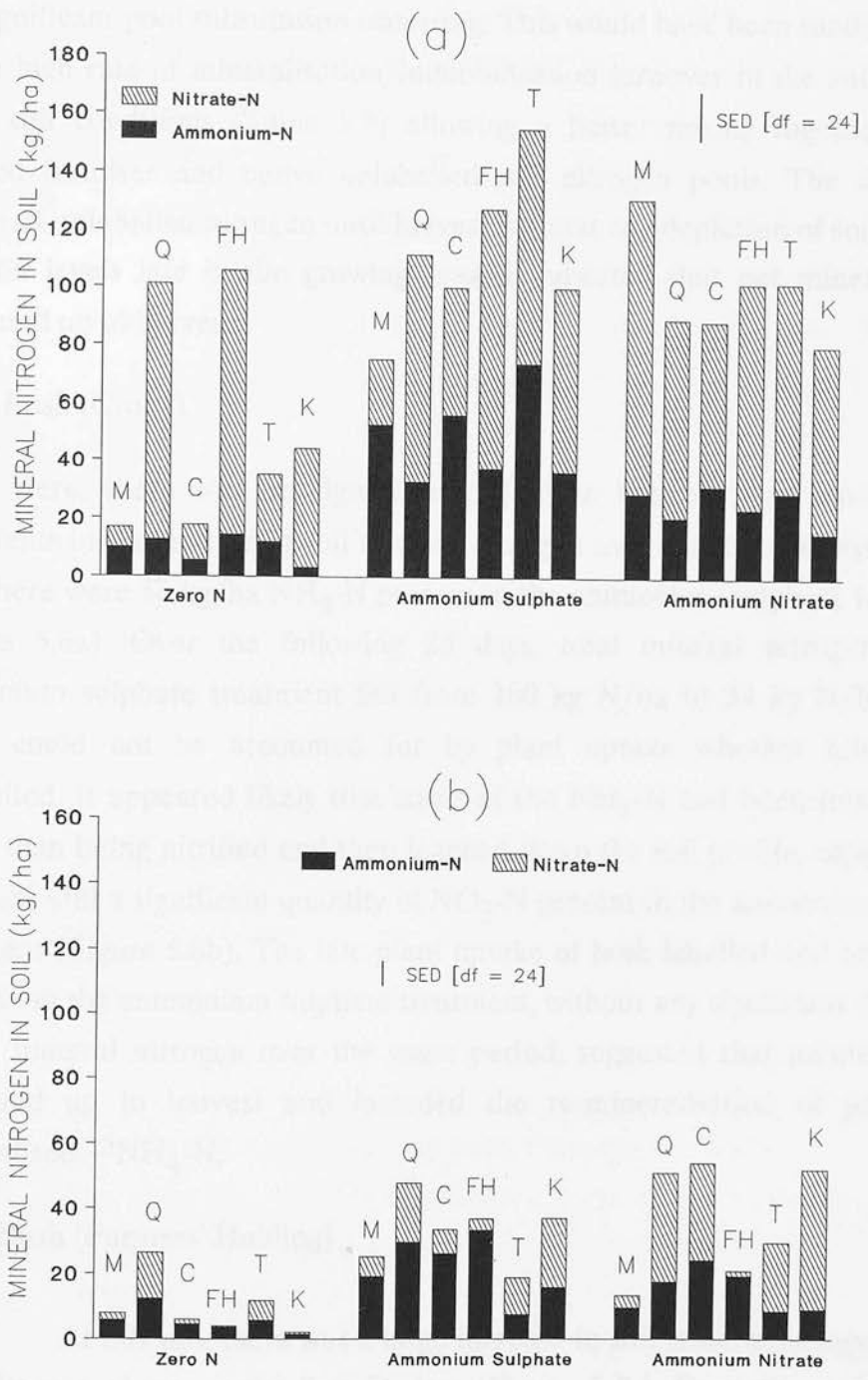


Figure 5.8. Quantities of nitrate- and ammonium-N in the soil at six sites in 1990 at first two sampling dates, under spring barley either unfertilised or given 120 kg N/ha at sowing, (a) 1st sampling and (b) 2nd sampling M- Manorhill; Q- Quixwood; C- Bush (Crofts) FH- Bush (Fm. Holding); T- Treaton; K- Kettle

respectively. Taking into account the low uptake of labelled nitrogen in the plant, and significant uptake of unlabelled nitrogen, it was probable that there was significant pool substitution occurring. This would have been made possible by the high rate of mineralisation/immobilisation turnover in the soil and the moist soil conditions (Table 5.3) allowing a better mixing together of the labelled fertiliser and native unlabelled soil nitrogen pools. The continued uptake of unlabelled nitrogen until harvest without any depletion of soil mineral nitrogen levels late in the growing season indicated that net mineralisation continued up to harvest.

5.2.3: Bush (Crofts)

Here, there was no significant difference between the two fertiliser treatments in the decline of soil mineral nitrogen over the first 54 days. At this time there were 56 kg/ha NH_4-N present in the ammonium sulphate treatment (Figure 5.8a). Over the following 28 days, total mineral nitrogen in the ammonium sulphate treatment fell from 100 kg N/ha to 34 kg N/ha, all of which could not be accounted for by plant uptake whether labelled or unlabelled. It appeared likely that some of the NH_4-N had been immobilised rather than being nitrified and then leached down the soil profile, especially as there was still a significant quantity of NO_3-N present in the ammonium nitrate treatment (Figure 5.8b). The late plant uptake of both labelled and unlabelled nitrogen in the ammonium sulphate treatment, without any significant depletion of soil mineral nitrogen over the same period, suggested that mineralisation continued up to harvest and included the re-mineralisation of previously immobilised $^{15}NH_4$-N.

5.2.4: Bush (Farmers' Holding)

At this site, there was a large increase in soil mineral nitrogen in the zero nitrogen plot over the first 51 days (Figure 5.7b). Over the same period there was no significant decline of mineral nitrogen in the ammonium sulphate treatment, but there was a drop of 47 kg N/ha in the ammonium nitrate treatment. Plant uptake of labelled nitrogen was greater in the ammonium nitrate treatment (Section 4.6.4), which could explain the greater decline of soil

Table 5.3: Soil moisture content over the growing season at six sites, 1990.

Manorhill	Date	25/3	14/5	8/6	10/7	8/8	SED
	Moisture (%)	18.8	17.0	13.6	17.0	9.8	(0.7)
Quixwood	Date	31/3	14/5	12/6	12/7	29/8	SED
	Moisture (%)	27.4	26.2	26.7	25.2	21.5	(0.9)
Bush (Crofts)	Date	30/3	23/5	21/6	16/7	27/8	SED
	Moisture (%)	24.7	21.6	17.9	24.5	19.5	(0.7)
Bush (Fm.Holding)	Date	2/4	23/5	21/6	16/7	20/8	SED
	Moisture (%)	24.3	26.2	17.0	23.3	24.5	(0.7)
Treaton	Date	28/3	17/5	19/6	17/7	22/8	SED
	Moisture (%)	27.4	25.8	21.5	23.6	26.0	(0.5)
Kettle	Date	25/4	4/6	25/6	19/7	31/8	SED
	Moisture (%)	18.2	15.2	17.5	11.7	13.4	(1.2)

(%) Moisture by weight (g/100g d.wt.)

mineral nitrogen in that treatment. However, the large accumulation of mineral nitrogen in the zero plot, and the significant uptake of unlabelled nitrogen in the plant, suggested that there was considerable microbial activity which could have affected the composition of the mineral nitrogen in the soil. By this time, 51 days after sowing, there were only 38 kg/ha NH_4-N remaining in the soil in the ammonium sulphate treatment, with the other 90 kg/ha as NO_3-N (Figure 5.8a). Over the following 29 days growth, there was a large fall in soil mineral nitrogen in all treatments which appeared to be mainly derived from the NO_3-N present with no significant change in the amount of NH_4-N (Figure 5.8b).

These losses were significantly greater than plant uptake of both labelled and unlabelled nitrogen. The late uptake of labelled nitrogen in the ammonium sulphate treatment appeared to be due to the higher levels of NH_4-N retained in the soil after 80 days growth. The loss of the NO_3-N could have been due to leaching down the profile or immobilisation. Over the period between 51 days and 80 days growth the soil was drying out rapidly (Table 5.2), and also given the heavier soil texture (Table 3.3) it seemed unlikely that there would be significant solute movement down the soil profile. Recous *et al.* (1988b) found that immobilisation in winter wheat increased up to the time of anthesis. Given the high microbial activity demonstrated by the rapid mineralisation in the zero plots, it is possible that NO_3-N was rapidly immobilised during this period and that the NH_4-N avoided this due to its reduced mobility in the drier soil conditions.

5.2.5: Treaton

Here, over the first 50 days growth there was a fall in the mineral nitrogen content in the ammonium nitrate treatment of 50 kg N/ha, whereas in the ammonium sulphate treatment there was no significant change. At this time there were 74 kg/ha and 30 kg/ha NH_4-N remaining in the ammonium sulphate and ammonium nitrate treatments, respectively (Figure 5.8a). Therefore, taking into account the low plant uptake of labelled nitrogen, approximately 50 % of the applied NH_4-N had either been nitrified or immobilised. There were 81 kg/ha and 73 kg/ha NO_3-N in the soil in the respective treatments. Over the next 33 days the amount of mineral nitrogen in the soil fell to 18 kg N/ha and 30 kg N/ha in the ammonium sulphate and ammonium nitrate treatments, respectively. Similarly to Farmers' Holding, the increased rate of plant uptake could not fully account for the decline in mineral nitrogen levels. Unlike Farmers' Holding, however, the soil remained quite moist throughout this period (Table 5.3) and the soil was light in texture and freely draining (Table 3.3). Therefore it was possible that there was some movement of nitrogen down the soil profile. This may explain the greater decline in the ammonium nitrate treatment over the first 50 days, despite the similar rate of plant uptake.

Even though a significant proportion of the NH_4-N in the ammonium sulphate treatment had been nitrified, there would have been a sufficient delay for most of this nitrogen still to be in the upper soil profile. The high levels of organic matter in the soil (Table 3.3) indicated that there was likely to be a significant rate of mineralisation/immobilisation turnover. Taking into account the late uptake of labelled nitrogen despite minimal levels of mineral nitrogen after 110 days growth, it appeared likely that there was significant immobilisation of labelled nitrogen between 50 and 83 days growth, some of which was re-mineralised later in the growing season. The greater decline of mineral nitrogen between 50 and 83 days in the ammonium sulphate treatment could possibly be attributed to the greater availability of NH_4-N at that time, both in terms of quantity and accessibility in the more moist soil compared with Farmers' Holding.

5.2.6: Kettle

Here, over the first 40 days there was a decline of approximately 50 kg N/ha in both fertiliser treatments. Over this period there was less than 10 kg/ha total nitrogen uptake in the plant (Section 4.6.6). The zero nitrogen treatment showed a rise of 20 kg N/ha over the same period indicating some net mineralisation. This nitrogen was virtually all present as NO_3-N (Figure 5.8a). Also, in the fertilised treatments most of the mineral nitrogen was in the NO_3-N form at this time. Therefore it appeared that most of the nitrogen lost from the soil mineral nitrogen pool up to this time had been as NH_4-N. Over the next 21 days there was a very large uptake of nitrogen in the plant tissues which was partly due to the late sowing of the crop, resulting in more rapid growth in the warmer conditions. The decline in soil mineral nitrogen indicated that there was very considerable net mineralisation. Despite a decline of only 40 kg N/ha in the zero nitrogen treatment, uptake in the plant over the same period was 86 kg N/ha. Similar amounts of unlabelled nitrogen were taken up in the fertilised treatments. It appeared that the rate of mineralisation was great enough to prevent mineral nitrogen levels in the fertilised plots falling below 40 kg/ha. At this time there was very little NH_4-N present in the soil (Figure 5.8b). Therefore, it appeared that the mineralised nitrogen was rapidly nitrified before

being taken up in the plant, although the light textured soil would have enabled greater root exploration. This would have resulted in greater competition between the roots and the nitrifying bacteria, allowing some of this mineralised nitrogen to be taken up as NH_4-N. This again indicated the high rates of microbial activity in the soil. The late uptake of labelled and unlabelled nitrogen indicated continued mineralisation up to harvest, some of which appeared to be the re-mineralisation of previously immobilised labelled fertiliser nitrogen.

5.3: Discussion

During the early stages of growth there were differences between sites with regard to soil mineral nitrogen levels. At most of the sites there was little change in mineral nitrogen levels over the first 50-60 days growth. However, at Middlestot and Upper Cairnie there were significant declines in soil mineral nitrogen over this period. At these two sites soil moisture contents were falling rapidly.

Neeteson *et al.* (1986), working on potatoes, suggested that rapid immobilisation of fertiliser nitrogen shortly after application was due to the uptake of nitrogen ions by micro-organisms, but that this uptake was into the vacuoles for the purpose of osmoregulation when under moisture stress, rather than being incorporated into the biomass structure itself. In their trials there was no moisture stress as the soils were near to field capacity, but they concluded that upon the dissolution of fertiliser granules the soil solution in the immediate vicinity would have high osmotic concentrations. It was also shown that most of this immobilised nitrogen reappeared over the next 5 weeks as the micro-organisms decomposed. By this time there would not have been such localised, highly concentrated solute pools and therefore no great further demand for nitrogen ions to act as an osmoticum. Similar results were reported under spring barley (Nielsen and Jensen, 1986), where up to 80 % of applied ammonium nitrate could not be detected in the soil nor in plant tissue within 12

days of application, but over the next 50 days growth at least 20-30 % of this nitrogen reappeared.

Under the dry soil conditions encountered at Middlestot and Upper Cairnie there would have been significant moisture stress after 50-60 days growth and therefore the reduced mineral nitrogen at these sites could be attributed to a greater accumulation of nitrogen in the micro-organisms.

There was a similar decrease in mineral nitrogen at Quixwood under more moist conditions. However, taking into account the high soil organic matter content and large net mineralisation in the zero nitrogen treatment, it is probable that there was significant mineralisation/immobilisation turnover which resulted in net immobilisation upon the addition of large quantities of mineral nitrogen.

At most sites, after 50-60 days growth there was a period of rapid decline which coincided with rapid plant uptake. However, at several of the sites plant uptake could not account for all of the mineral nitrogen decline. Recous *et al.* (1988b) reported increased rates of immobilisation up to anthesis in winter wheat. It was suggested that this increase was correlated to available carbon, which would have been exuded from plant roots into the rhizosphere during plant development. Wheatley *et al.* (1990) showed that, after a 10 week pot experiment growing unfertilised barley plants, increased carbon in the rhizosphere exuded from developing plant roots resulted in a doubling of the accumulated nitrogen in the microbial biomass.

This may have contributed to the rapid decline in mineral nitrogen that was recorded. There may also have been some leaching down the soil profile, and while there was some evidence of increasing mineral nitrogen in the 20-40 cm soil layer, the rapid decline in mineral nitrogen was occurring at a time of decreasing soil moisture contents and therefore leaching losses at this time were probably quite small.

There was no such rapid decline in the ammonium sulphate treatment at Middlestot, or in any of the fertiliser treatments at Upper Cairnie. It appeared that the reduced mobility of the NH_4-N at Middlestot resulted in greater retention in the soil. At Upper Cairnie the soil was drying out more rapidly and this appeared to greatly reduce the mobility of NO_3-N also. Bergstrom (1986) reported that under moist conditions the uptake of calcium nitrate fertiliser by spring barley was rapid, after a stable period of one month after sowing during early crop development. It was also noted that there was reduced uptake and greater retention of mineral nitrogen in the soil under drier soil conditions in the spring.

At all sites, other than Middlestot and Upper Cairnie, the quantity of mineral nitrogen in the soil levelled off at values equal to or lower than pre-fertilisation levels from around 80-100 days after sowing. This tended to coincide with the peak uptake of labelled nitrogen in the crop. Mineral nitrogen values in the soil remained constant from then until harvest despite the continued uptake of unlabelled nitrogen in the crop. This indicated that there was net mineralisation continuing up to harvest, and that this therefore could be an important factor in determining the total nitrogen uptake in the crop.

6: THE USE OF A ^{15}N POOL DILUTION TECHNIQUE TO CALCULATE THE GROSS RATES OF SOIL NITROGEN TRANSFORMATIONS

6.1: Introduction

In the results described in the previous sections all mention of mineralisation and immobilisation referred to the net effect of either process on the overall increase or decrease of mineral nitrogen in the soil. These net effects would also have been affected by the rates of nitrification and the plant uptake of nitrogen. Therefore it is very difficult to estimate the actual gross rates of these inter-related soil processes from the data presented.

Methods for calculating gross rates of these soil transformations have been proposed using ^{15}N pool dilution techniques (Kirkham and Bartholomew, 1954, 1955; Barraclough, 1988). These methods have been used here to calculate gross rates of mineralisation, immobilisation, nitrification and also the relative proportions of nitrogen uptake derived from the NH_4-N and NO_3-N pools, respectively. The necessary measurements were made using a method proposed by Barraclough and Smith (1987) and Barraclough (1988). The method involves the application of single-labelled $^{15}NH_4{}^{14}NO_3$ and $^{14}NH_4{}^{15}NO_3$ to paired microplots; by measuring the decline in the ^{15}N pool in each microplot it is possible to calculate the gross rates for the soil nitrogen transformation processes (Section 2.5.2.5). The aim of the experiments was to try to determine the rates of the interacting soil transformation processes and relate them to the uptake of fertiliser and soil nitrogen in the crop. In 1989, measurements were taken over three periods during the growing season: germination/seedling emergence, stem elongation and grain filling. In 1990, measurements were only taken during stem elongation, during which time a significant proportion of total nitrogen uptake occurs, to determine whether the rates of soil nitrogen transformations during this period would explain differences in fertiliser and soil nitrogen uptake over a wider range of sites.

6.2: Results and Discussion

The results presented in this section refer to measurements made at the two field sites in 1989 and the six field sites in 1990. Details of each site can be found in Tables 3.1 and 3.3.

6.2.1: Mineralisation

The calculated gross mineralisation rates at different stages of growth at Bush in 1989 are shown in Figure 6.1. Over the growing season, there was a slight rise in the rate of mineralisation. In early April, during the period of growth immediately after sowing, the rate of mineralisation was 1.2 kg N/ha/d. By June, during the period of stem elongation the rate of mineralisation increased to 1.4 kg N/ha/d, then rose again to 1.6 kg N/ha/d by late July. The relative amounts of NH_4-N and NO_3-N in the applied fertiliser did not have any significant effect on the rates of mineralisation at any time during the growing season. The measurements taken in July were restricted to plots receiving equal proportions of NH_4-N and NO_3-N, due to a lack of space for any further treatments.

At Upper Cairnie (Figure 6.2) there was greater variation in the gross rates of mineralisation at different stages of the growing season than there had been at the Bush site. During the period of growth immediately after sowing there was considerably lower mineralisation than at Bush with a rate of only 0.5 kg N/ha/d. By June, the rate of mineralisation had risen to 1.2 kg N/ha/d, before rising to a much higher rate of 3.2 kg N/ha/d in July. The general increases in mineralisation throughout the growing season at both Upper Cairnie and Bush can probably be attributed to increases in soil temperatures caused by the warmer climatic conditions later in the summer. Nishio and Fujimoto (1989) found that the major factor controlling gross mineralisation, in soils either fallow or cropped with maize, was temperature. They found that the highest rates were observed in July.

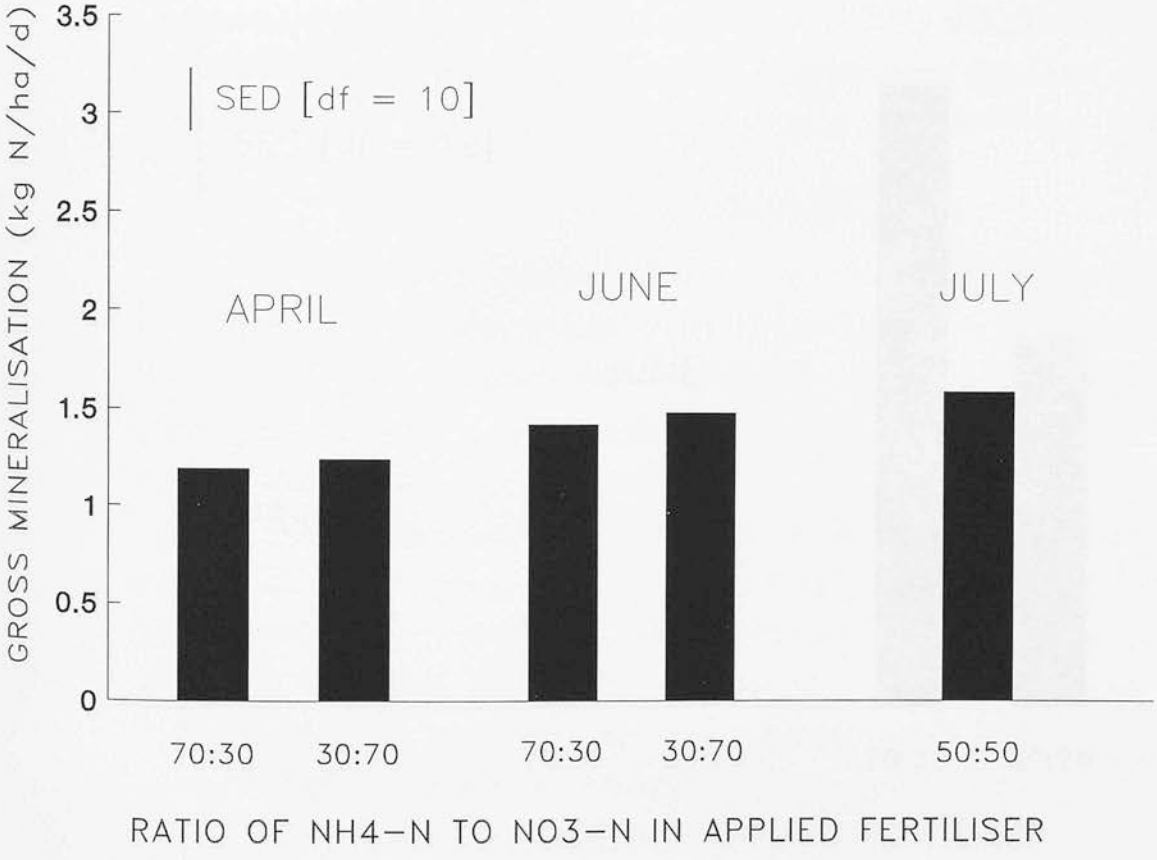


Figure 6.1. Gross mineralisation rate (kg N/ha/d) at three stages of growth in spring barley fertilised with differing ratios of NH_4-N and NO_3-N, Bush (March Park) 1989.

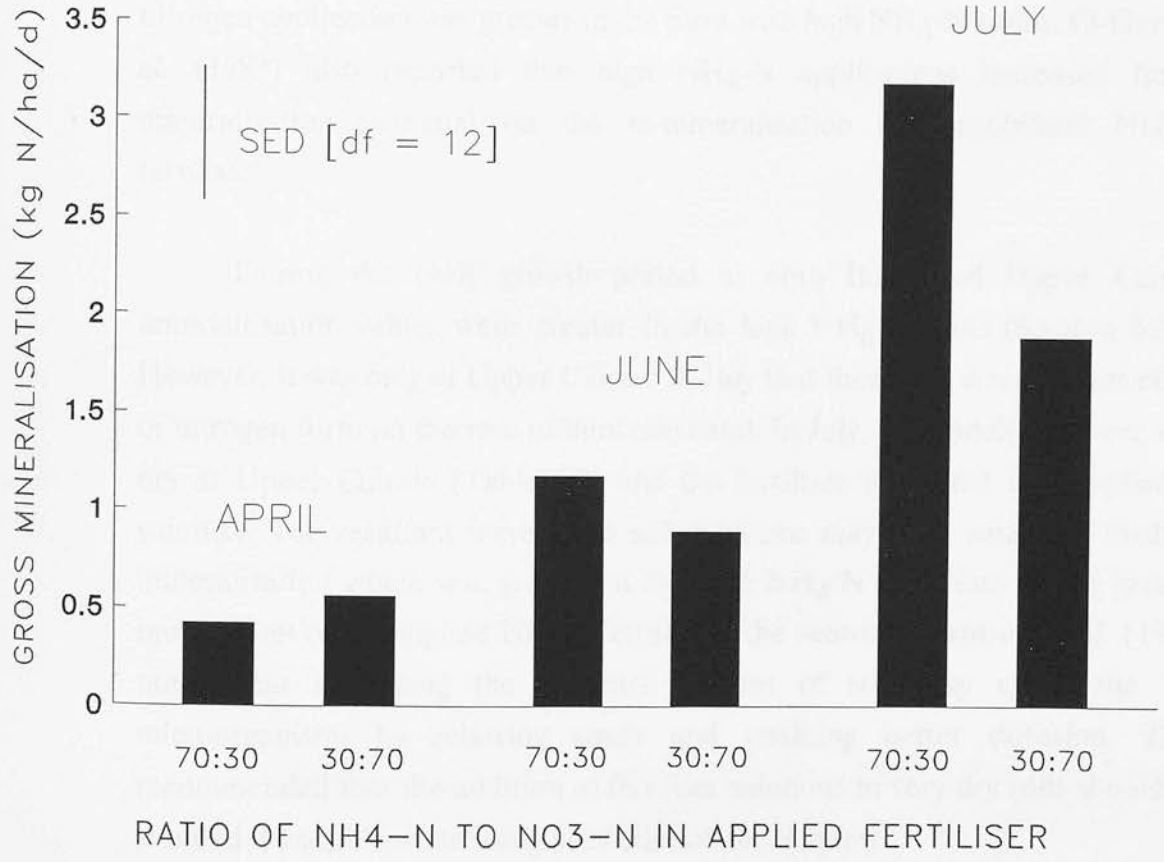


Figure 6.2. Gross mineralisation rate (kg N/ha/d) at three stages of growth in spring barley fertilised with differing ratios of NH_4-N and NO_3-N, Upper Cairnie 1989.

At Upper Cairnie the relative amounts of NH_4-N and NO_3-N applied as fertiliser also had a significant effect on the rate of mineralisation. In the early growth period there was no difference in the rates of mineralisation of the two forms of nitrogen, but during later growth in July the rate of mineralisation was 3.2 kg N/ha/d when the fertiliser applied was 70 % NH_4-N compared to 1.9 kg N/ha/d when there was an application of 70 % NO_3-N. Geens *et al.* (1991) found that the form of applied nitrogen did not affect the rate of mineralisation in the early part of the growing season, but measurements taken later in the season showed that plots which received high ratios of NH_4-N to NO_3-N showed increased rates of mineralisation. This was attributed to the re-mineralisation of the initial applications of fertiliser nitrogen which had initially been immobilised. They also found that the rate of immobilisation of this initial nitrogen application was greater in the plots with high NH_4-N ratios. El-Haris *et al.* (1983) also reported that high NH_4-N applications increased future mineralisation potential via the re-mineralisation of immobilised NH_4-N fertiliser.

During the early growth period at both Bush and Upper Cairnie immobilisation values were greater in the high NH_4-N plots (Section 6.3.3). However, it was only at Upper Cairnie in July that there was a significant effect of nitrogen form on the rate of mineralisation. In July, soil conditions were very dry at Upper Cairnie (Table 5.2) and the fertiliser treatment was applied in solution. The resultant increase in soil moisture may have caused a flush of mineralisation which was greater in the high NH_4-N plots due to the greater immobilisation of applied NH_4-N earlier in the season. Davidson *et al.* (1991) noted that increasing the moisture content of soil may affect the soil microorganisms by relieving stress and enabling better diffusion. They recommended that the addition of fertiliser solutions to very dry soils should be avoided if possible when using pool dilution techniques.

In 1990, measurements were restricted to the period of time covering stem elongation, and also restricted to one treatment of equal proportions of NH_4-N and NO_3-N fertiliser; the focus of the work was the measurement of the inherent differences in the rates of soil transformations between the six sites.

Gross rates of mineralisation (Figure 6.3) ranged from 1.1 kg N/ha/d at Manorhill to 2.2 kg N/ha/d at Kettle. In general, the rates of mineralisation reflected the organic matter contents of the soils, with higher rates of mineralisation at Quixwood and Treaton compared to Manorhill or Farmers Holding. The only exception was at Kettle, where mineralisation rates were highest despite having the lowest organic matter content. However, plant uptake of nitrogen was greatest at this site, most notably unlabelled nitrogen (Section 4.6.5), and this appeared to be due to the mineralisation of crop residues from the previous season which were brussels sprouts. This suggests that even if upward movement of NO_3-N from the subsoil contributed to the overall uptake of unlabelled nitrogen at this site (Section 4.4), mineralisation of crop residues still contributed significantly to the soil nitrogen pool, and this was not detected by the hot KCl extraction technique which measured potentially mineralisable nitrogen (Section 6.2.1).

6.2.2: Nitrification

The calculated rates of nitrification at different stages during the growing season at Bush and Upper Cairnie in 1989 are shown in Figures 6.4 and 6.5, respectively. At Bush the rate of nitrification in the high NH_4-N treatments remained constant in April and June at a rate of 2 kg N/ha/d. This was significantly lower than the rates in the high NO_3-N treatments which were 5.5 kg N/ha/d in April, falling to 2.7 kg N/ha/d in June. It might have been expected that nitrification rates in the high NH_4-N treatments would have been equal to, if not higher than the rates in the high NO_3-N treatments because of the higher levels of available NH_4-N substrate.

One possible reason for the observed effects could be the inhibition of nitrification in the presence of high NH_4-N concentrations which have been reported in a number of papers. The NH_4-N concentration which inhibited nitrification has varied. Malhi and McGill (1982) reported that inhibition occurred as the NH_4-N concentration increased from 200 μg N/g to 300 μg N/g. Nishio and Fujimoto (1990) reported maximum nitrification rates occurred at 300 μg N/g with reduced rates above this concentration. However, Darrah *et al.*

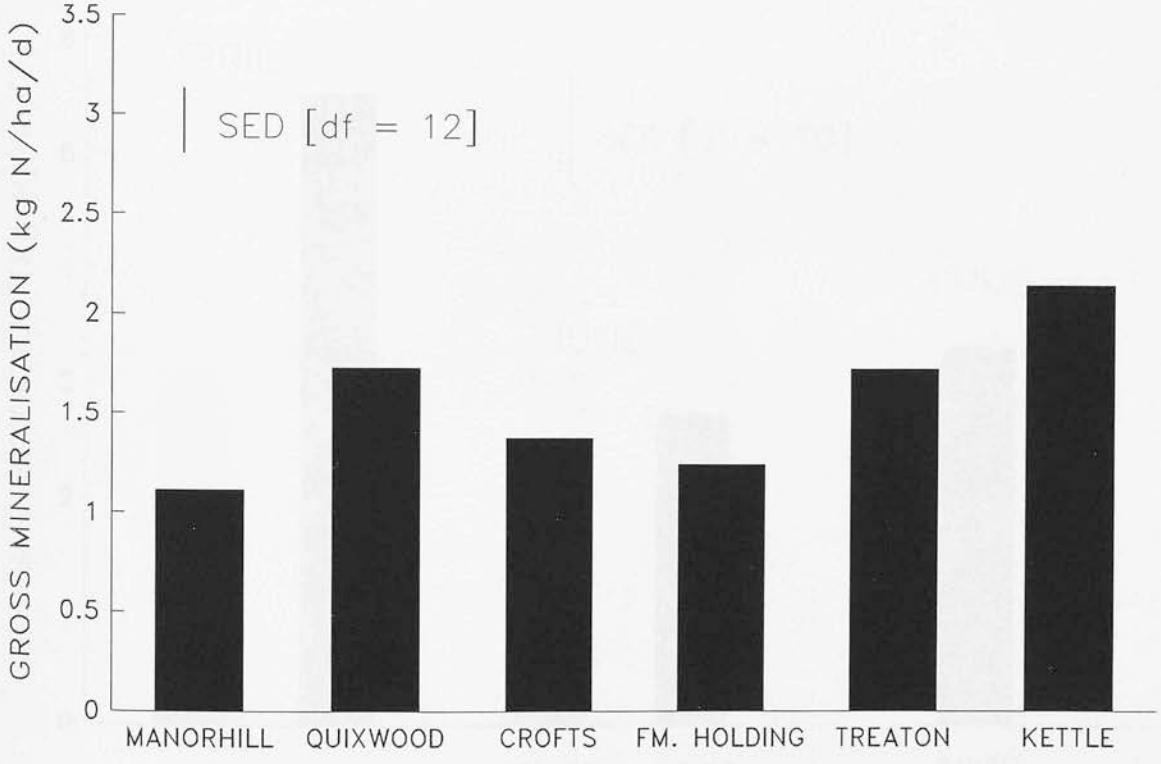


Figure 6.3. Gross mineralisation rate (kg N/ha/d) during stem elongation in spring barley fertilised with equal amounts of NH_4-N and NO_3-N, at six sites, 1990.

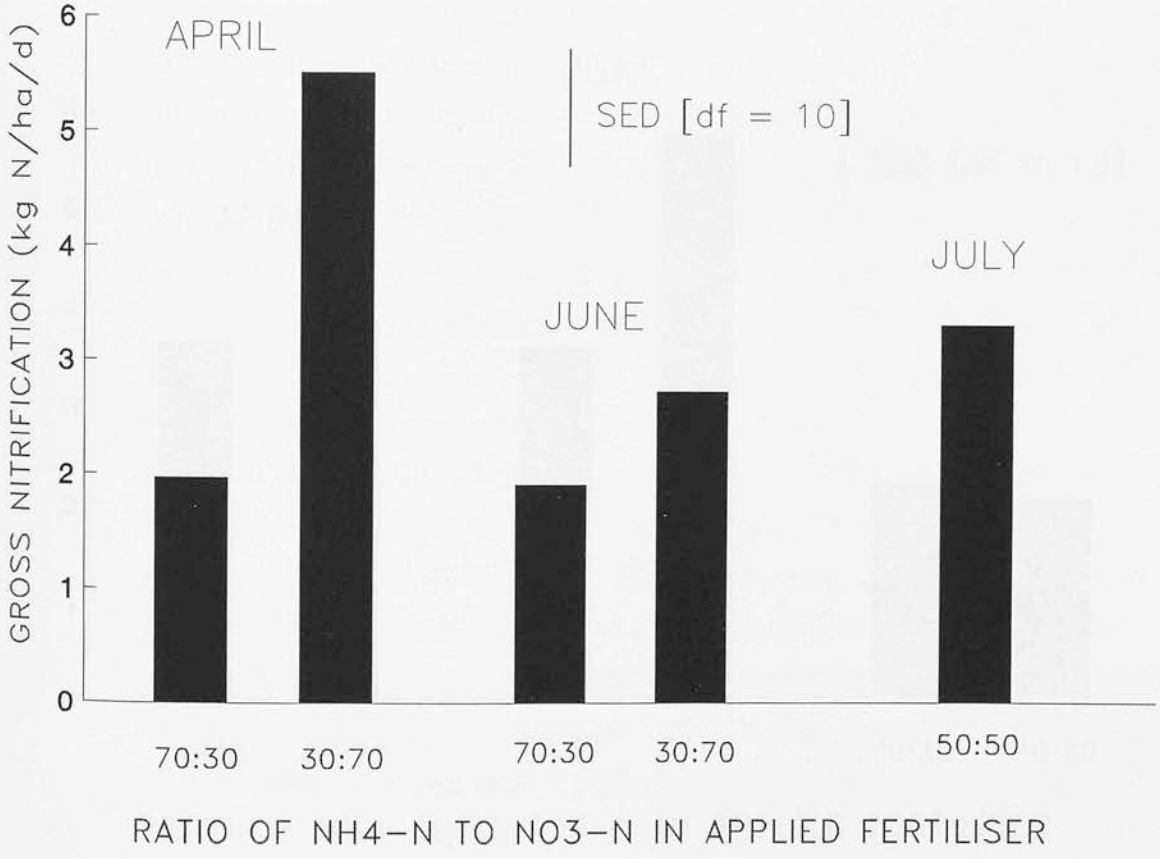


Figure 6.4. Gross nitrification rate (kg N/ha/d) at three stages of growth in spring barley fertilised with differing ratios of NH_4-N and NO_3-N, Bush (March Park) 1989.

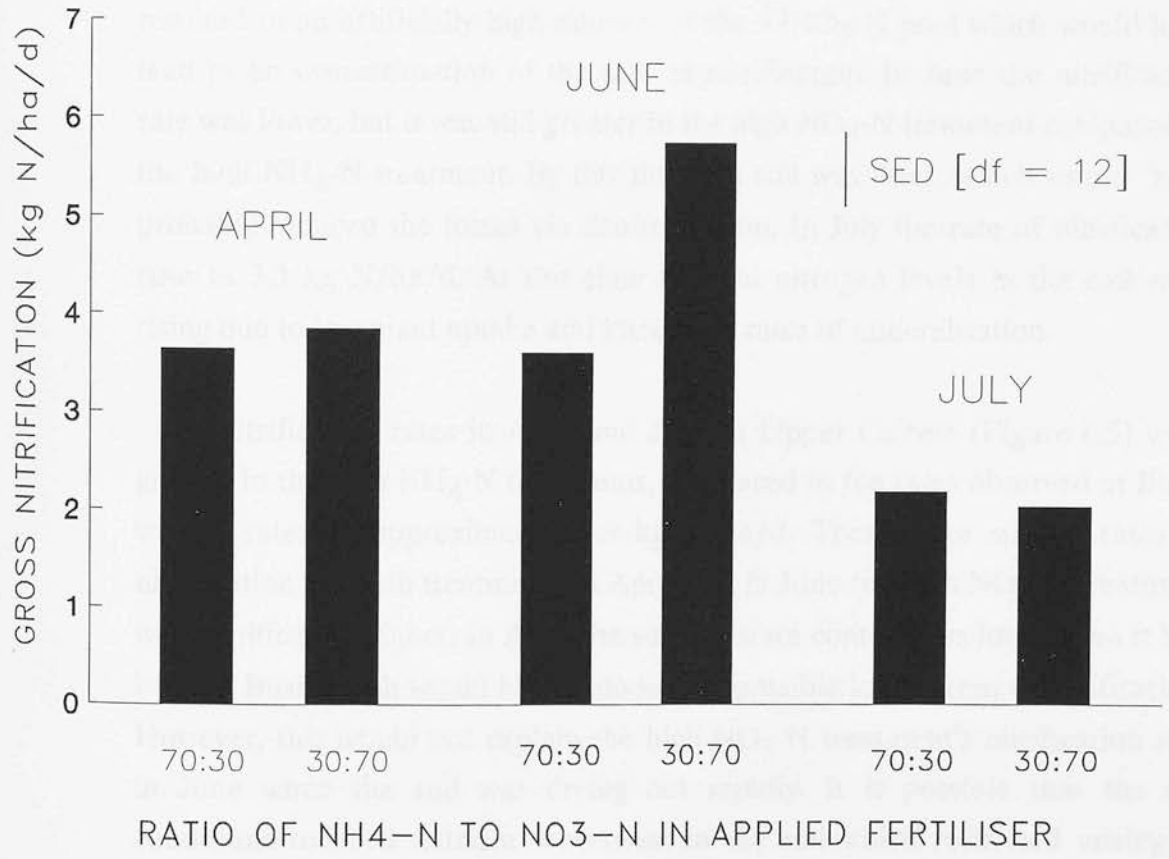


Figure 6.5. Gross nitrification rate (kg N/ha/d) at three stages of growth in spring barley fertilised with differing ratios of NH_4-N and NO_3-N, Upper Cairnie 1989.

(1985) did not report significant inhibition of nitrification until concentrations reached 700 μg N/g. All of these concentrations however, were much greater than the 84 kg NH_4-N applied in the high ammonium treatments. Therefore it would appear unlikely that concentrations could have been great enough to induce significant inhibition of nitrification.

Another possible explanation for the observed differences between the treatments could be related to the fate of the NO_3-N applied to these plots. In April the soil moisture content was high and therefore there may have been losses of nitrogen via denitrification. If this occurred as the ^{15}N fertiliser was applied there could have been disproportionately high losses of $^{15}NO_3$-N fertiliser compared to the losses of $^{14}NO_3$-N in the soil. This would have resulted in an artificially high dilution of the $^{15}NO_3$-N pool which would have lead to an overestimation of the rate of nitrification. In June the nitrification rate was lower, but it was still greater in the high NO_3-N treatment compared to the high NH_4-N treatment. By this time the soil was drier, which would have probably reduced the losses via denitrification. In July the rate of nitrification rose to 3.3 kg N/ha/d. At this time mineral nitrogen levels in the soil were rising due to low plant uptake and increasing rates of mineralisation.

Nitrification rates in April and June at Upper Cairnie (Figure 6.5) were greater in the high NH_4-N treatments, compared to the rates observed at Bush, with a rates of approximately 3.6 kg N/ha/d. There were similar rates of nitrification for both treatments in April, but in June the high NO_3-N treatment was significantly higher. In April the soil moisture content was lower than it had been at Bush which would have reduced the possible losses from denitrification. However, this would not explain the high NO_3-N treatment's nitrification rate in June when the soil was drying out rapidly. It is possible that the dry conditions reduced nutrient movement in the soil which restricted mixing of fertiliser and soil nitrogen pools, and that during a period of rapid nitrogen uptake this nitrogen was supplied mainly from the applied fertiliser nitrogen. This may also explain the very low values for the uptake of NH_4-N in June at Upper Cairnie (Section 6.2.4). By July, nitrification had been reduced to about 2 kg N/ha/d in both treatments. A reduction in the nitrification rate might have

been expected at this time because of the low levels of mineral nitrogen in the soil. However, the rate of mineralisation was greatest at this time (Section 6.2.1). Therefore sufficient NH_4-N would have been produced to sustain a higher rate of nitrification. It is possible that the very dry soil conditions meant that not all of this NH_4-N was actually available to the soil nitrifiers because of reduced nutrient mobility in the soil.

In 1990, the rate of nitrification during stem elongation ranged from 3 kg N/ha/d at Quixwood to 4 kg N/ha/d at Kettle (Figure 6.6). Over the first few weeks of growth, the reduction in the amount of NH_4-N in the soil was much greater than the reduction of NO_3-N, which suggested that significant rates of nitrification were occurring (Section 5.2). During the period of stem elongation the amounts of NH_4-N and NO_3-N in the soil were reduced to very low levels, due to nitrification and plant uptake. The high nitrification values suggest that much of the NH4-N was nitrified before it was taken up by the crop. The higher nitrification value at Kettle may have been due to the light textured, well aerated soil structure, but also may have been partly the result of upward movement of NO_3-N from the subsoil diluting the $^{15}NO_3$-N applied (Section 4.2).

6.2.3: Immobilisation

The calculated values for gross rates of immobilisation at each of the sites studied in 1989 and 1990 are shown in Tables 6.1-6.3. In this method, the rates of immobilisation were derived from the calculated values for mineralisation, nitrification, the uptake of NH_4-N in the plant and the rate of decline of NH_4-N in the soil. Therefore errors in any of these other parameters would also have an effect on values for immobilisation. The majority of the values in Tables 6.1-6.3 show negative immobilisation rates. This should not be possible because these are supposed to be gross rates. It appears that there may have been several factors, with varying degrees of influence at different stages during the growing season, which could have caused negative immobilisation values.

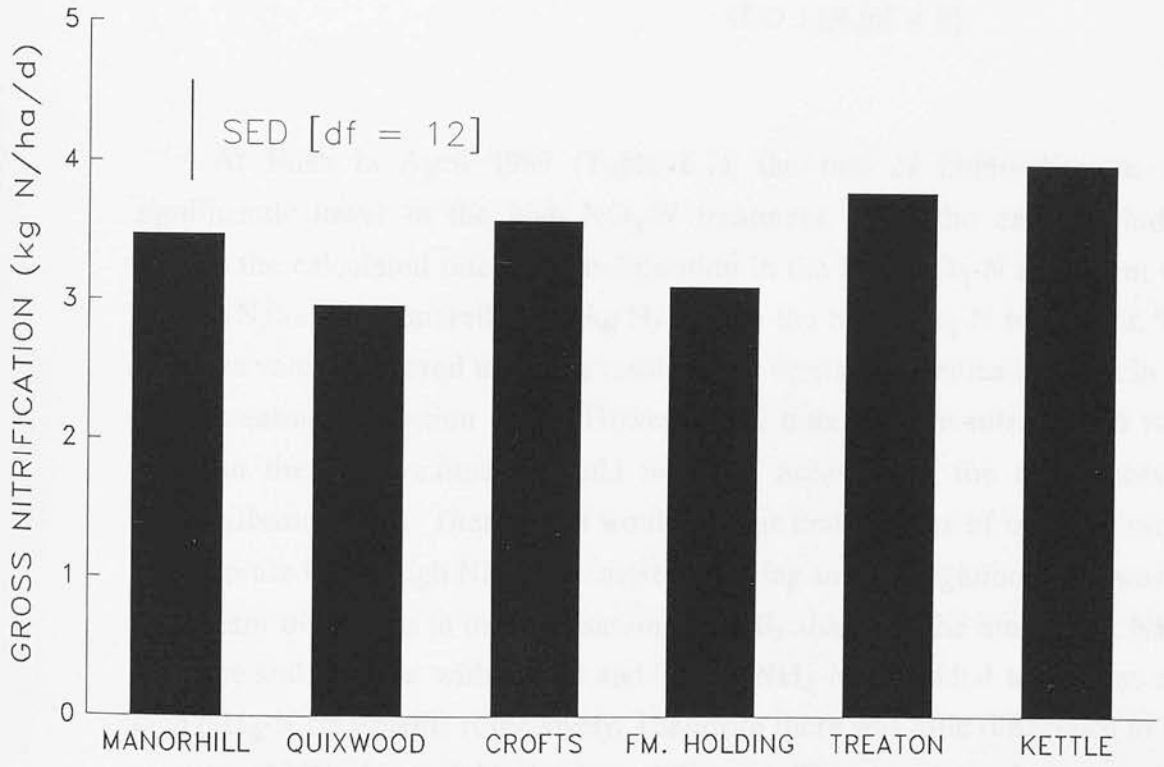


Figure 6.6. Gross nitrification rate (kg N/ha/d) during stem elongation in spring barley fertilised with equal amounts of NH_4-N and NO_3-N, at six sites, 1990.

Table 6.1: Calculated rates of gross immobilisation (kg N/ha/d) over three growth periods with varying ratios of ammonium-N to nitrate-N fertiliser applied, Bush (Lower Fulford) 1989.

Growth Period	NH_4-N : NO_3-N		
	70:30	30:70	50:50
Emergence	1.86	-3.80	--
Stem elongation	-1.33	-1.61	--
Maturation	--	--	-2.58

SED 1.09 [df = 8]

At Bush in April 1989 (Table 6.1), the rate of immobilisation was significantly lower in the high NO_3-N treatment. Over the early period of growth the calculated rate of immobilisation in the high NO_3-N treatment was -3.8 kg N/ha/d, compared to 1.9 kg N/ha/d in the high NH_4-N treatment. The negative value appeared to be the result of the very high nitrification rate in the same treatment (Section 6.2.2). However, the difference in nitrification rates between the two treatments could not fully account for the differences in immobilisation rates. Therefore it would appear that the rate of immobilisation did increase in the high NH_4-N treatment. During stem elongation there was no significant difference in immobilisation rates. By this time the amount of NH_4-N in the soil was low with only 3 and 7 kg $^{15}NH_4$-N/ha added to the low and high NH_4-N treatments respectively. Therefore there was little difference in the amount of NH_4-N available for immobilisation. The negative values were due to the fact that the nitrification rates were still higher than the combined rates of mineralisation and the daily decline of NH_4-N in the soil, which was small over this period.

At Upper Cairnie (Table 6.2), the rate of immobilisation was significantly greater in the high NH_4-N treatment during the period of growth after sowing. This was associated with an unusually high nitrification rate in the low NH_4-N

Table 6.2: Calculated rates of gross immobilisation (kg N/ha/d) over three growth periods with varying ratios of ammonium-N to nitrate-N fertiliser applied, Upper Cairnie 1989.

Growth Period	NH_4-N : NO_3-N	
	70:30	30:70
Emergence	-0.81	-2.60
Stem elongation	-2.52	-5.75
Maturation	0.76	-1.20

SED 1.19 [df = 12]

treatment, which could have been the result of significant denitrification losses of the added ^{15}N fertiliser (Section 6.2.2). However, it should be noted that there was no direct measurement of denitrification. During stem elongation immobilisation was higher in the high NH_4-N treatment. The difference between the two rates was similar to the difference in nitrification rates. As discussed earlier (Section 6.3.2) these nitrification rates appeared quite high, possibly as a result of incomplete mixing of the fertiliser and soil nitrogen pools leading to a disproportionately high uptake of $^{15}NO_3$-N during a period of rapid plant uptake. During the later growth period in July, immobilisation rates were higher as a result of lower nitrification rates and an increase in the rates of mineralisation.

In 1990 immobilisation rates were higher at Treaton, Quixwood and Crofts compared to the other sites (Table 6.3). Soil organic matter contents were also higher at these sites, which might indicate a higher microbial population available for immobilisation. The lowest rate of immobilisation was at Kettle, where there was a large uptake of soil nitrogen (Section 4.4). This suggested that there was a high rate of net mineralisation of the nitrogen, presumably as a consequence of the brussels sprout crop residues from the previous season.

Table 6.3: Calculated rates of gross immobilisation (kg N/ha/d) during the period of stem elongation, after application of ammonium nitrate fertiliser at six sites, 1990.

Site	Immobilisation
Manorhill	-2.52
Quixwood	-1.74
Bush (Crofts)	-1.82
Bush (Farmers Holding)	-2.07
Treaton	-1.55
Kettle	-2.82

SED 0.85 [df = 12]

All of the immobilisation rates in 1990 were negative. It is doubtful whether the calculated rates of nitrification could have been sufficiently overestimated to account fully for the negative immobilisation values. However, if there was some overestimation of rates of nitrification, and this was taken in conjunction with an underestimation of the rates of mineralisation, and of the rate of NH_4-N decline, then this could possibly account for the negative values. Such a combination could occur if there was not a good mixing of the soil nitrogen pool and the applied fertiliser ^{15}N. The effects of poor mixing on the overestimates of nitrification rates were discussed in Section 6.2.2. The rate of mineralisation could have been underestimated in the $^{15}NH_4$-N microplots because of the reduced dilution of the applied $^{15}NH_4$-N. This could occur because, although any mineralisation would add $^{14}NH_4$-N to the total nitrogen pool, poor mixing would mean that immobilisation would be predominantly $^{14}NH_4$-N instead of a mixture of both $^{15}NH_4$-N and $^{14}NH_4$-N from a well mixed nitrogen pool. Therefore the dilution of $^{15}NH_4$-N would be slowed down. Plant uptake would also be mainly of $^{14}NH_4$-N, which would have the same effect. There might also be a reduction in the real rate of immobilisation because of a reduced amount of NH_4-N substrate. This would be more

important when large amounts of $^{15}NH_4$-N were applied, such as in the sowing applications in 1989, rather than the small additions in the later growth stages either in 1989 or 1990. Due to the short-term nature of these pool dilution experiments, slow mixing of the two mineral nitrogen pools could result in quite large errors in the calculated rates of the soil processes, as appears to have occurred in the calculated immobilisation rates which resulted from an accumulation of the errors from the other calculated rates.

6.2.4: Percentage plant uptake as ammonium-N and nitrate-N

The results in this section were calculated using data from the $^{15}NO_3$-N microplots. The percentage uptake from the NH_4-N pool was calculated by difference, because data calculated directly from the $^{15}NH_4$-N microplots would include ^{15}N applied as $^{15}NH_4$-N but taken up as $^{15}NO_3$-N due to nitrification.

At Bush in 1989, over 70 % of nitrogen uptake immediately after sowing was from the nitrate pool in both treatments (Figure 6.7). Total nitrogen uptake was low during this period, with only 13 kg N/ha and 15 kg N/ha taken up in the high NH_4-N and high NO_3-N treatments, respectively. Therefore there were sufficient applications of the more mobile NO_3-N in both treatments to accommodate this uptake by seedlings with limited root growth. During stem elongation, uptake from the nitrate pool was greater in the high NO_3-N treatment. In both treatments over 70 % of the uptake was from the nitrate pool, as in the previous growth period. This indicated that nitrifiers were converting a high proportion of the NH_4-N produced via mineralisation to NO_3-N before it was taken up by the plant. The amount of both NO_3-N and NH_4-N in the soil was greatly reduced by this time. It was not possible to calculate uptake data for the period before harvest, because there was a net loss of nitrogen from the crop which invalidated the equations used.

At Upper Cairnie (Figure 6.8), the calculated uptake from the nitrate pool was only 10 % in both treatments. Therefore it appeared that 90 % of nitrogen uptake was derived from the ammonium pool. However, when uptake was

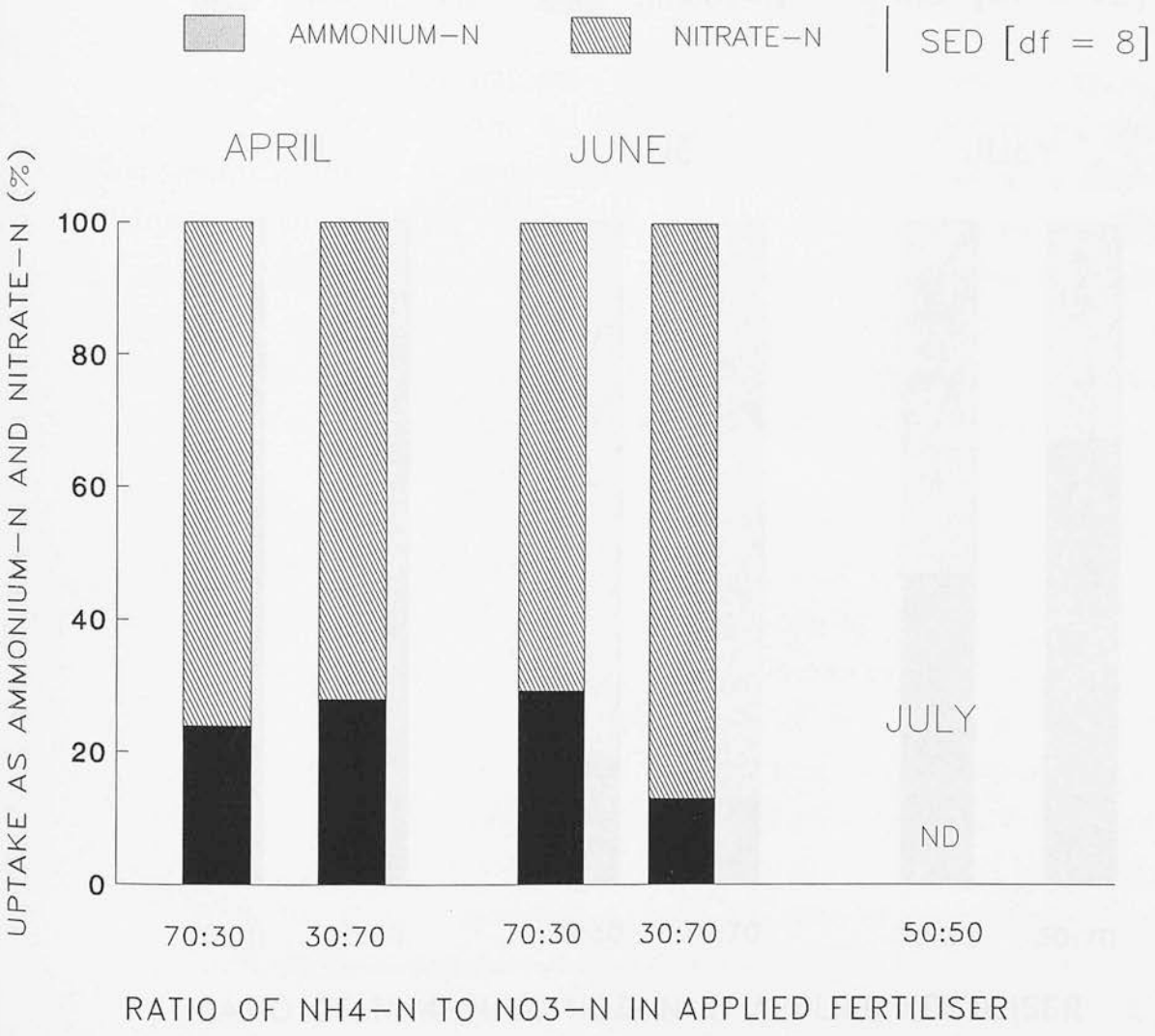


Figure 6.7. Percentage nitrogen uptake as NH_4-N and NO_3-N at three stages of growth in spring barley fertilised with differing ratios of NH_4-N and NO_3-N, Bush (March Park) 1989.

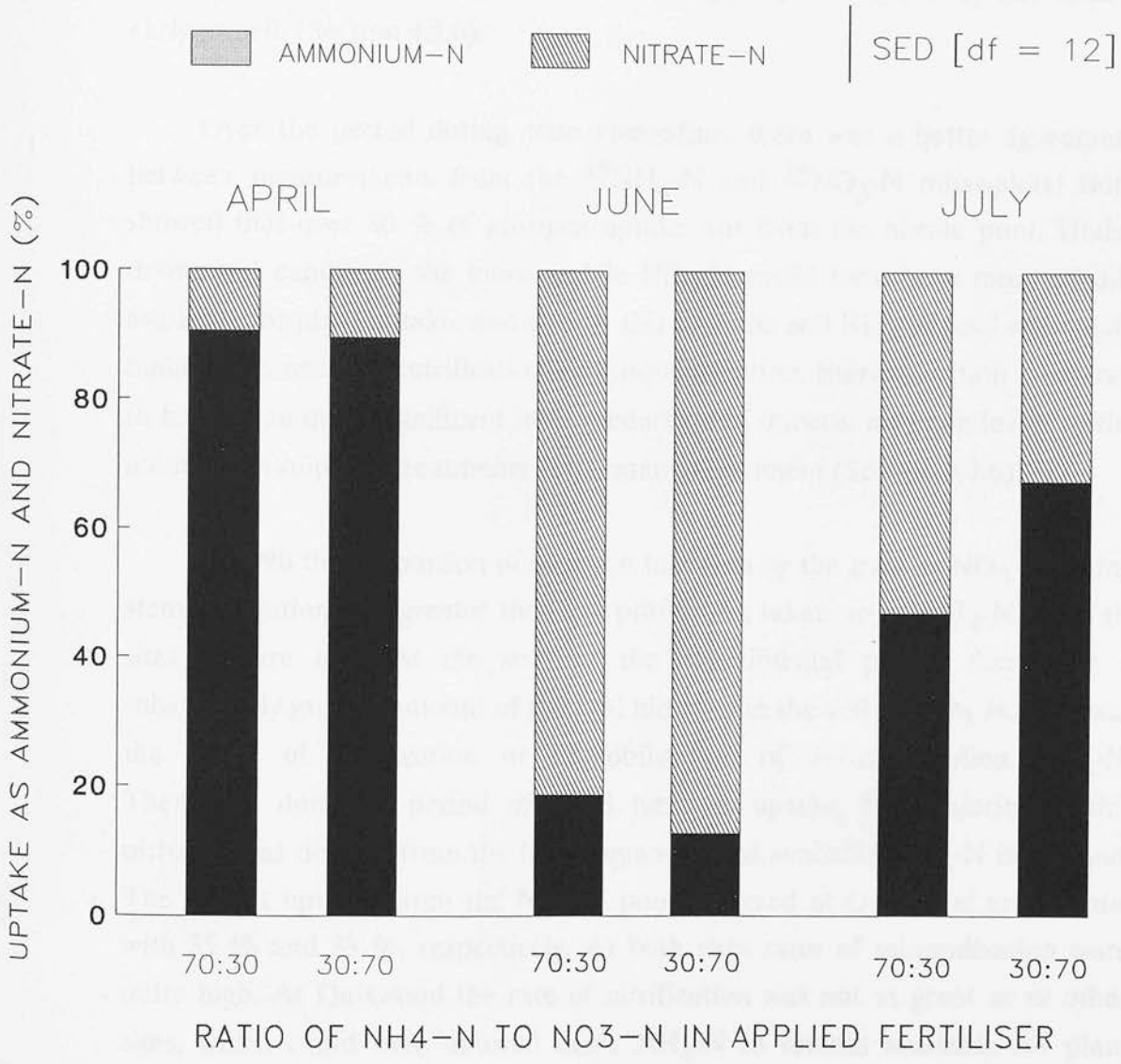


Figure 6.8. Percentage nitrogen uptake as NH_4-N and NO_3-N at three stages of growth in spring barley fertilised with differing ratios of NH_4-N and NO_3-N, Upper Cairnie 1989.

calculated using data from the $^{15}NH_4$-N microplots, uptake from the ammonium pool was reduced to < 5 %, even though this might have overestimated uptake by including $^{15}NH_4$-N which was nitrified to $^{15}NO_3$-N prior to uptake. It was apparent that very little ^{15}N had been taken up by the plants in either treatment. This suggested that there was poor mixing of the fertiliser and soil nitrogen pools. Plant uptake data showed that soil nitrogen contributed much more than fertiliser nitrogen to total plant uptake during early growth (Section 4.5.6).

Over the period during stem elongation, there was a better agreement between measurements from the $^{15}NH_4$-N and $^{15}NO_3$-N microplots. Both showed that over 80 % of nitrogen uptake was from the nitrate pool. Under drying soil conditions the more mobile NO_3-N would have been more readily available for plant uptake, and also by this time the soil NH_4-N pool was small, mainly as a result of nitrification and immobilisation. Immobilisation appeared to have been quite significant in the reduction of mineral nitrogen levels in the ammonium sulphate treatments in the main experiment (Section 5.1.6).

In 1990 the proportion of nitrogen taken up by the crop as NO_3-N during stem elongation was greater than the proportion taken up as NH_4-N at all six sites (Figure 6.9). At the start of the experimental period there was a substantially greater amount of mineral nitrogen in the soil as NO_3-N. This was the result of nitrification or immobilisation of earlier applied NH_4-N. Therefore, during a period of rapid nitrogen uptake, the majority of this nitrogen was derived from the larger quantities of available NO_3-N in the soil. The largest uptakes from the NH_4-N pool occurred at Quixwood and Kettle, with 35 % and 33 %, respectively. At both sites rates of mineralisation were quite high. At Quixwood the rate of nitrification was not as great as at other sites, which could have allowed more NH_4-N to remain available for plant uptake. At Kettle the rate of nitrification was higher. However, the light soil texture might have allowed greater root exploration which could have resulted in greater competition between the roots and the nitrifying bacteria for mineralised NH_4-N. Such an effect could explain the greater plant uptake from the NH_4-N pool at this site.

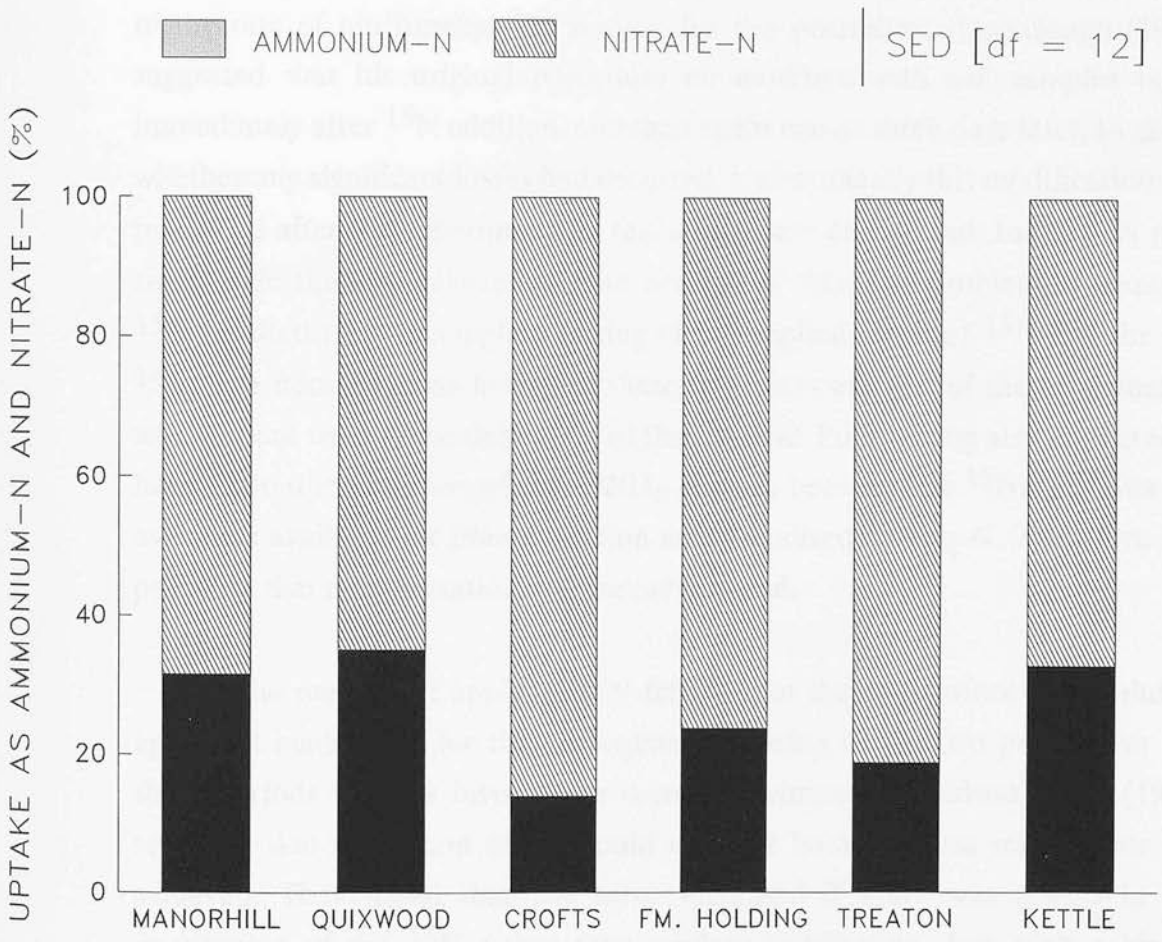


Figure 6.9. Percentage nitrogen uptake as NH_4-N and NO_3-N during stem elongation in spring barley fertilised with equal amounts of NH_4-N and NO_3-N, at six sites, 1990.

6.2.5: Problems encountered with the application of the method

There were several factors, related to the application of the method used, which appeared to have influenced these results. All of the calculated rates were derived from measurement of the dilution of the applied ^{15}N. Therefore any errors related to these values could significantly affect calculated results. The apparent losses of $^{15}NO_3$-N, possibly due to denitrification, appeared to significantly affect the $^{15}NO_3$-N pool size, leading to overestimates of the rate of nitrification. To account for this possibility, Barraclough (1991) suggested that his original procedure be modified with soil samples taken immediately after ^{15}N addition, and then again two or three days later, to assess whether any significant losses had occurred. Unfortunately this modification was published after the experiments in this thesis were carried out. Initial ^{15}N pool sizes could then be adjusted to take account of this. The problem of losses of ^{15}N resulted from incomplete mixing of the applied fertiliser ^{15}N and the soil ^{14}N. The homogeneous mixing of these two pools was one of the fundamental assumptions used in the derivation of this method. Poor mixing also appeared to have limited the dilution of the $^{15}NH_4$-N pool, because this $^{15}NH_4$-N was not as widely available for immobilisation as mineralised $^{14}NH_4$-N. Therefore it is probable that mineralisation was underestimated.

The method of applying ^{15}N fertiliser to the soil surface as a solution appeared inadequate for the homogeneous mixing of the two pools, over the short periods of time involved in these experiments. Davidson *et al.* (1991) reported that significant errors could occur if homogeneous mixing was not achieved. They found that this error increased if there was a bias in the distribution of the ^{15}N rather than random distribution. Just such a biased vertical distribution could have occurred after the addition of $^{15}NH_4$-N to the soil surface. Barraclough (1991) suggested that the ^{15}N should be injected to various depths in the soil to improve the mixing of the two nitrogen pools.

Such a method of application would also have resolved another problem which occurred during applications over the later growth periods, especially when the plants were fully grown. It proved difficult to apply the ^{15}N solution to

the soil evenly throughout the microplot because of the presence of the plants. During the application, some of the solution landed on plant tissue, and it is probable that not all of this was washed off into the soil. ^{15}N pool sizes in the plant tissues over the last growth period at Bush in July 1989 were higher than expected during a period of less rapid nitrogen uptake. This resulted in a large overestimate of uptake from the NO_3-N pool in some of the replicates at Bush in 1989. Similarly, if $^{15}NH_4$-N microplot data was used for the calculation instead, then there was an overestimate of uptake from the NH_4-N pool. Recous *et al.* (1988b) reported that foliar absorption of ^{15}N applied to the soil in the form of a spray, during stem elongation in winter wheat, increased apparent uptake of fertiliser nitrogen. There was not such a significant problem at Upper Cairnie. This was probably due to the fact that lower dry matter yields meant that plants were smaller and less densely packed, making ^{15}N applications easier.

A related problem at Bush was the fact that, in two of the replicates, there was a reduction in plant nitrogen over the period of the experiment in July. This meant that it was not possible to calculate the proportion of ^{15}N in the plant nitrogen uptake over that period. At Upper Cairnie, plant nitrogen increased in all the replicates, due to low losses of nitrogen from the plants during the later growth stages (Section 4.5.6). However, by this time changes in plant nitrogen were not large compared to the total plant nitrogen content, which meant that there was a large multiplication factor involved in the calculation. The use of data, from dry matter cuts taken outside the microplots, may have introduced spatial variability and resulted in errors in plant nitrogen contents. Late in the growing season, when changes in plant nitrogen contents over time were small, such errors could have been highly significant. This would have a large effect on the multiplication factor and therefore on the proportions of nitrogen uptake from each pool. For these reasons this method of Barraclough (1988, 1991) does not appear suitable for the assessment of the sources of nitrogen uptake late in the growing season.

6.3: Conclusions

The aim of this experiment was to assess the rates of individual soil processes over a range of sites, and at different stages during the growing season. The results showed that, in general, rates of mineralisation increased during the growing season, as soil temperatures increased. This would have maintained the availability of soil nitrogen for plant uptake during the later stages of growth. The calculated rates of nitrification were generally high, which indicated that NH_4-N was quite quickly converted to NO_3-N. Values for the proportions of plant uptake from the two nitrogen pools tended to confirm this. However, the problems which were encountered using this method (Barraclough, 1988, 1991) resulted in some large errors, most notably in the calculated rates of immobilisation. These errors could possibly be overcome by a better immediate mixing of the soil N and applied fertiliser ^{15}N.

7: THE PREDICTION OF POTENTIALLY AVAILABLE SOIL NITROGEN USING TWO SIMPLE CHEMICAL EXTRACTION TECHNIQUES

7.1: Introduction

The ability to predict the likely quantity of mineral nitrogen which will be mineralised from the soil organic matter and be available for plant uptake is of great importance in agriculture. With such information there can be better management of fertiliser N applications with resulting benefits in terms of economics, the environment and product quality of crops such as malting barley.

Many biological and chemical predictive methods have been proposed, of which there have been extensive reviews (Bremner, 1965; Keeney, 1982b; Stanford, 1982). Good correlations have generally been found with the use of biological incubation methods when compared to plant uptake in pot experiments, but less satisfactory correlations have been found with field data (Keeney, 1982a). However, because of the complexity and time-consuming nature of biological incubations it is recognised that a simple chemical soil test would be the preferred option for regular laboratory use.

Recently chemical methods have been developed using KCl as a hydrolysing agent to estimate the likely release of soil nitrogen from a range of soils (Øien and Selmer-Olsen, 1980; Whitehead, 1981; Gianello and Bremner, 1986a). The accuracy of these methods has been tested against results from biological incubation tests (Selmer-Olsen *et al.*, 1981; Gianello and Bremner, 1986b), or with the uptake of nitrogen in pot experiments with oat plants (Øien and Selmer-Olsen, 1980), or with rye-grass (Whitehead, 1981).

The aims of this experiment were to compare the results obtained with two variants of the KCl hydrolysis method, and other soil factors such as organic matter content and mineral nitrogen content in the profile at sowing, with the uptake of soil N in spring barley as determined with the use of ^{15}N fertiliser.

7.2: Results and Discussion

Tables 3.1 and 3.3 (Section 3) give details of the physical and chemical properties of the soils used in this investigation, from 10 sites in Eastern Scotland.

7.2.1: Chemical extraction methods

The measured potentially available soil organic nitrogen, as determined by the two KCl extraction methods, is shown in Table 7.1. The more concentrated extracting solution and longer boiling of the Gianello method released nearly double the amount of nitrogen compared to the Whitehead method. Also shown is the % organic matter in each soil, as this has also been recommended as a measure of potentially available soil nitrogen (Keeney, 1982b).

The results in Table 7.2 show the mean values for each site of the amount of soil nitrogen uptake in the above-ground tissues of the whole plant, and also in the grain only. The mean % N in the grain at a fertiliser rate of 120 kg N/ha is also shown. The uptake of soil nitrogen from the Upper Cairnie and Kettle soils was higher than expected, based on the predictions of the KCl extraction methods. These two soils differed from the others in terms of cropping history (Tables 3.1 and 3.3). This classified them as N-Index 1 soils (SAC, 1985), which should have a larger pool of potentially mineralisable organic nitrogen derived from the previous year's crop residues than the remainder which were classified as N-index zero. However, neither the results of the KCl extraction methods nor the measure of soil organic matter appeared to account for this enhanced nitrogen uptake.

At Kettle, the mineralisation of crop residues from the previous season contributed significantly to soil nitrogen uptake. The residues were brussels sprouts, which would have had a low C:N ratio. In the well aerated soil at Kettle this could have induced a large net mineralisation rate. Another contribution may have derived from high concentrations of NO_3-N below

Table 7.1: Estimated potentially available nitrogen released by the two chemical extraction methods and measure of soil organic matter content.

Site	Gianello & Bremner (kg/ha)	Whitehead (kg/ha)	Organic Matter[a] (%)
Bush (Lower Fulford)	78.7	43.2	3.7
Middlestot	60.3	27.2	2.3
Bush (March Park)	71.4	43.6	3.4
Up.Cairnie	47.1	22.2	1.8
Manorhill	55.1	25.6	2.4
Quixwood	89.0	44.8	5.1
Bush (Crofts)	79.3	52.6	4.7
Bush (Fm.Holding)	67.9	43.7	3.3
Treaton	74.4	41.5	5.7
Kettle	51.5	21.0	2.8

[a] Method of Allison (1965).

Table 7.2: Soil nitrogen[1] uptake by spring barley at harvest in grain, whole plant (above ground) and % grain N when 120 kg N/ha fertiliser N applied.

Site	Soil N in Grain (kg/ha)	Soil N in Plant (kg/ha)	Grain N (%)
Bush (Lower Fulford)	43.2	66.0	1.66
Middlestot	30.0	41.1	1.28
Bush (March Park)	48.2	57.0	1.87
Up.Cairnie	43.2	46.1	2.02
Manorhill	35.6	47.2	1.75
Quixwood	57.4	78.5	1.83
Bush (Crofts)	55.6	71.3	1.71
Bush (Fm.Holding)	40.1	49.1	1.43
Treaton	32.2	41.1	1.61
Kettle	82.6	122.8	1.91

[1] difference between total plant N and ^{15}N uptake.

sampling depth (30 cm), that were not detected, and which became available for plant uptake at this site. High nitrate concentrations could have resulted from the large fertiliser nitrogen applications in previous years, to a site, which, in two of the previous four years had been sown with vegetable crops. Therefore, it is possible that the very high uptake of soil nitrogen at this site was derived from both of these sources, neither of which were accounted for in the KCl extractions.

At Upper Cairnie there was no history of intensive horticultural cropping. Soil nitrogen uptake was not very high due to the very dry soil conditions which reduced yields and nitrogen uptake (Section 4.1, 4.2). Even so, the soil nitrogen uptake was still higher than expected from the results of the KCl extraction method. This appeared to be the result of mineralisation of the oil seed rape residues from the previous season. It is probable that soil nitrogen uptake would have been higher under more moist soil conditions, which would have further reduced the accuracy of the KCl extraction method at this site. Therefore the relationships between the quantities of nitrogen released by the KCl extraction and the measured soil nitrogen uptake were calculated excluding the two Index 1 soils, and are shown in Figures 7.1-7.5. The correlation coefficients are presented in Table 7.3.

Figures 7.1 and 7.2 show the relationship between the soil nitrogen uptake in above-ground plant tissue and nitrogen extracted by the Gianello and Whitehead methods, respectively. The Gianello method showed a significant correlation, and proved to be the more accurate in its predictions. Similar results were obtained by Gianello and Bremner (1986b) who found that the best correlations between chemical methods and biological incubations were obtained with methods where the extracting solutions were heated for 4 hours or longer. Hong *et al.* (1990) carried out a series of comparisons between chemical indexes and nitrogen availability in fields cropped with corn and did not find a very strong relationship. However, the majority of these fields had been manured for several years or previously cropped with grass or legumes, and would therefore have been, in the ADAS system, designated as Index 1 or 2 soils. Similarly, in this work, the results at Upper Cairnie and Kettle did not fit

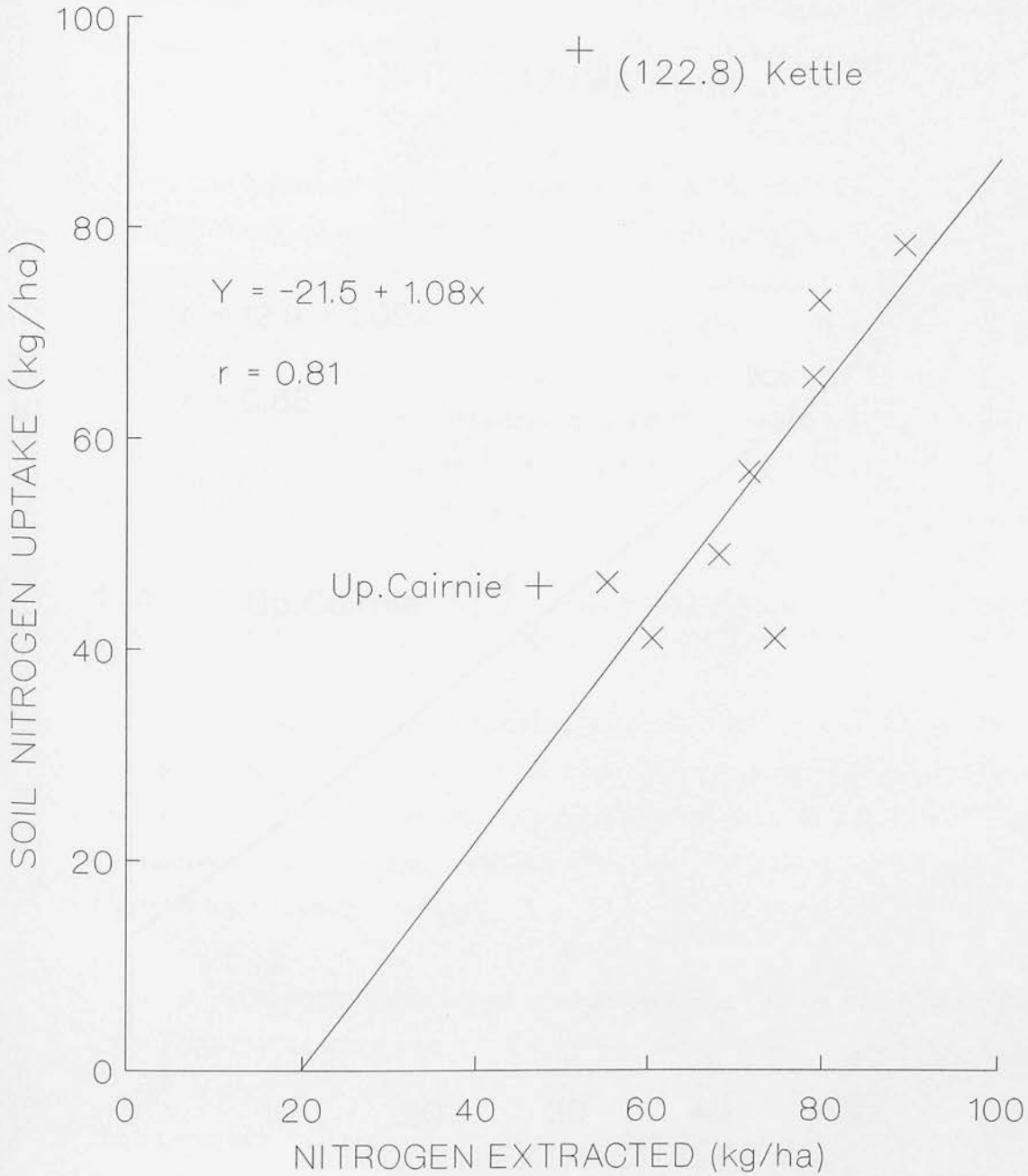


Figure 7.1. Relationship between nitrogen extracted by the Gianello and Bremner method and soil nitrogen uptake in above ground plant tissue. (Relationship excludes data from Upper Cairnie and Kettle).

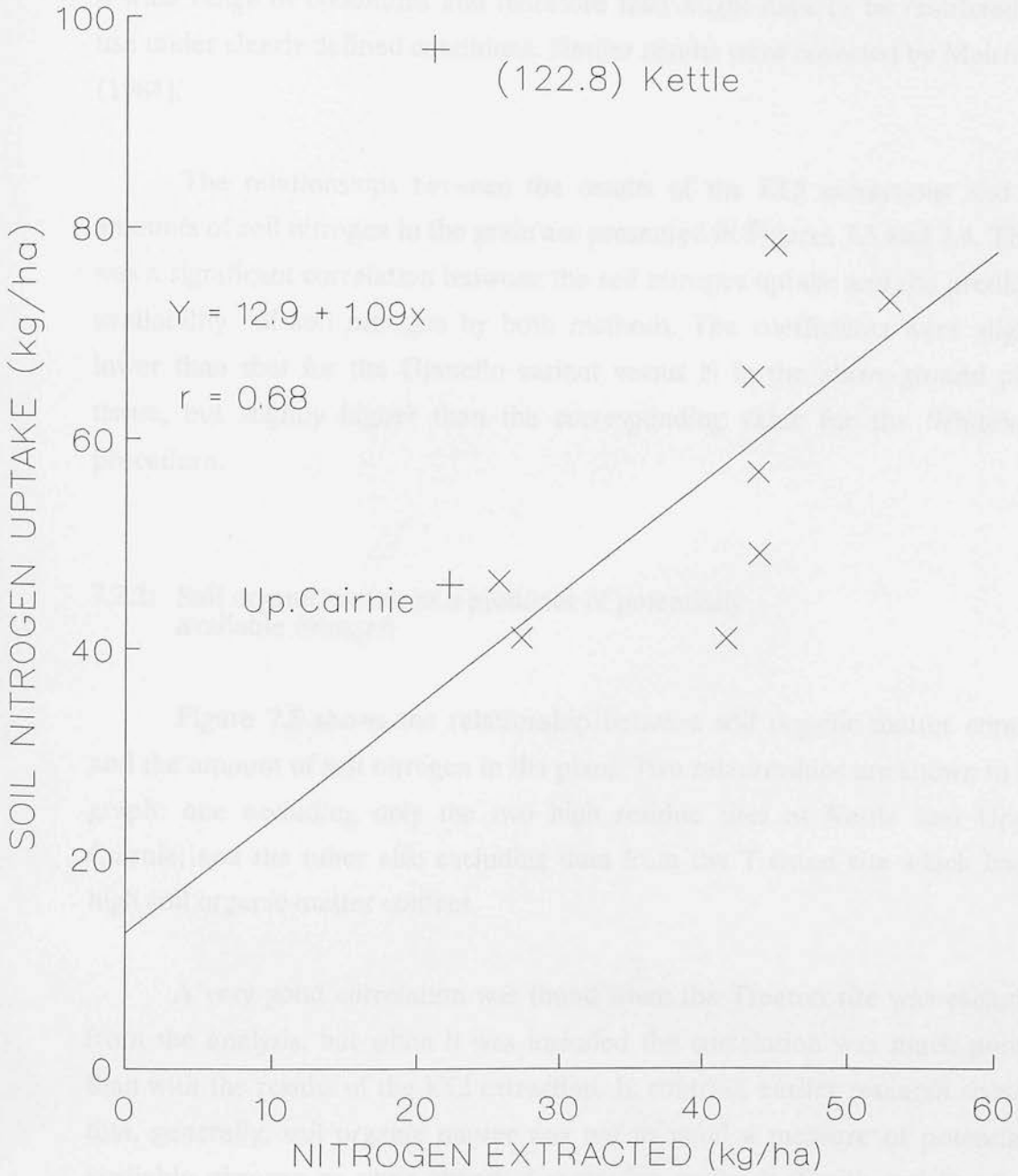


Figure 7.2. Relationship between nitrogen extracted by the Whitehead method and soil nitrogen uptake in above ground plant tissue. (Relationship excludes data from Upper Cairnie and Kettle).

the relationships described above, and the soils at these sites were also the only ones which were not Index zero soils. It seems likely that the technique is only applicable to Index zero soils. Fox and Piekielek (1984) found that predictions using chemical indexes were improved when soils which were previously cropped with legumes were excluded from the relationships. They concluded that it may not be possible for any one test to predict nitrogen availability under a wide range of conditions and therefore tests might have to be restricted for use under clearly defined conditions. Similar results were reported by Meisinger (1984).

The relationships between the results of the KCl extractions and the amounts of soil nitrogen in the grain are presented in Figures 7.3 and 7.4. There was a significant correlation between the soil nitrogen uptake and the predicted availability of soil nitrogen by both methods. The coefficients were slightly lower than that for the Gianello variant versus N in the above-ground plant tissue, but slightly higher than the corresponding value for the Whitehead procedure.

7.2.2: Soil organic matter as a predictor of potentially available nitrogen

Figure 7.5 shows the relationship between soil organic matter content and the amount of soil nitrogen in the plant. Two relationships are shown in the graph: one excluding only the two high residue sites at Kettle and Upper Cairnie, and the other also excluding data from the Treaton site which had a high soil organic matter content.

A very good correlation was found when the Treaton site was excluded from the analysis, but when it was included the correlation was much poorer than with the results of the KCl extraction. In contrast, earlier research showed that, generally, soil organic matter was not as good a measure of potentially available nitrogen as some chemical extraction methods (Smith and Stanford, 1971; Gianello and Bremner, 1986b).

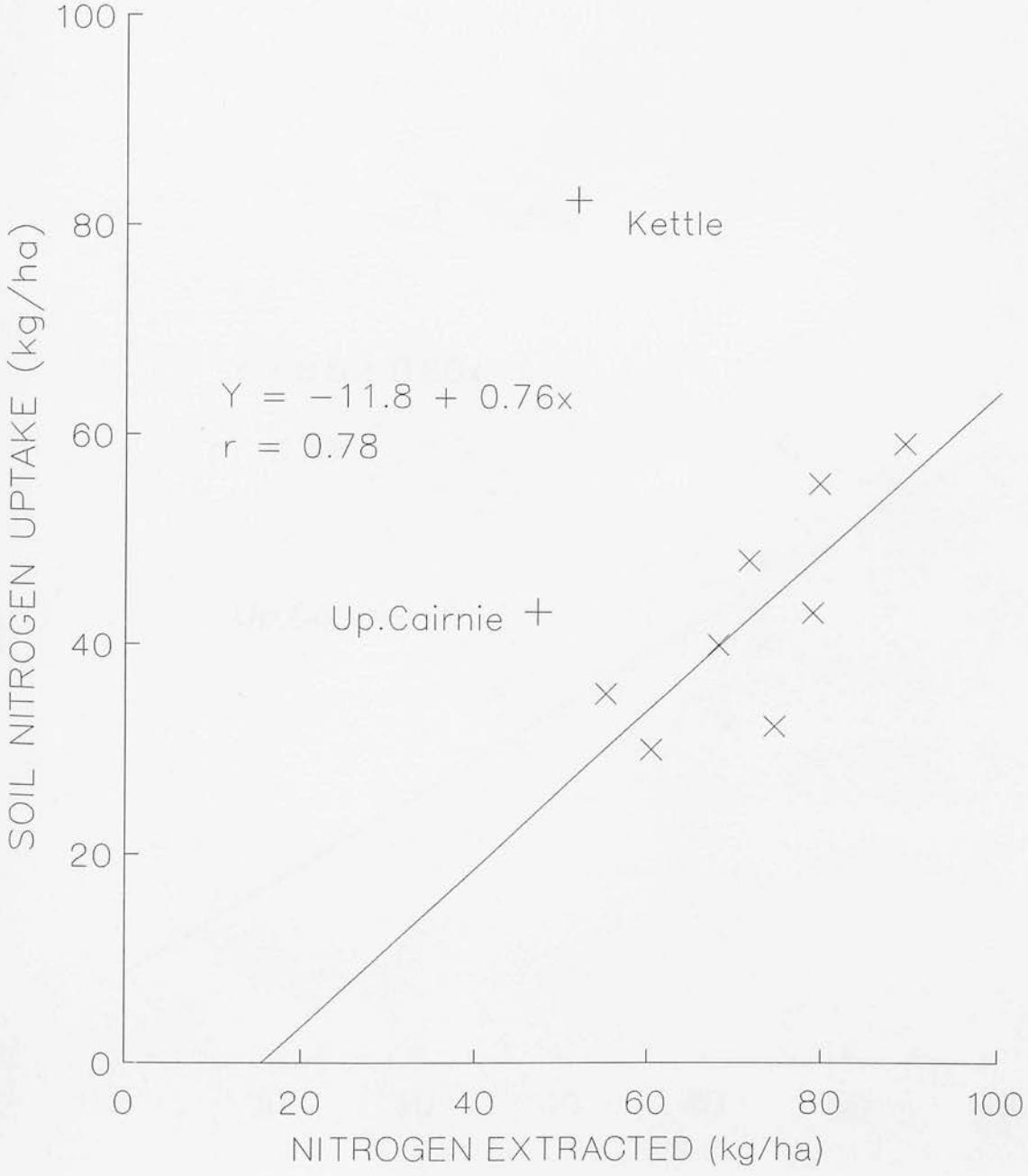


Figure 7.3. Relationship between nitrogen extracted by the Gianello and Bremner method and soil nitrogen uptake in the grain only. (Relationship excludes data from Upper Cairnie and Kettle).

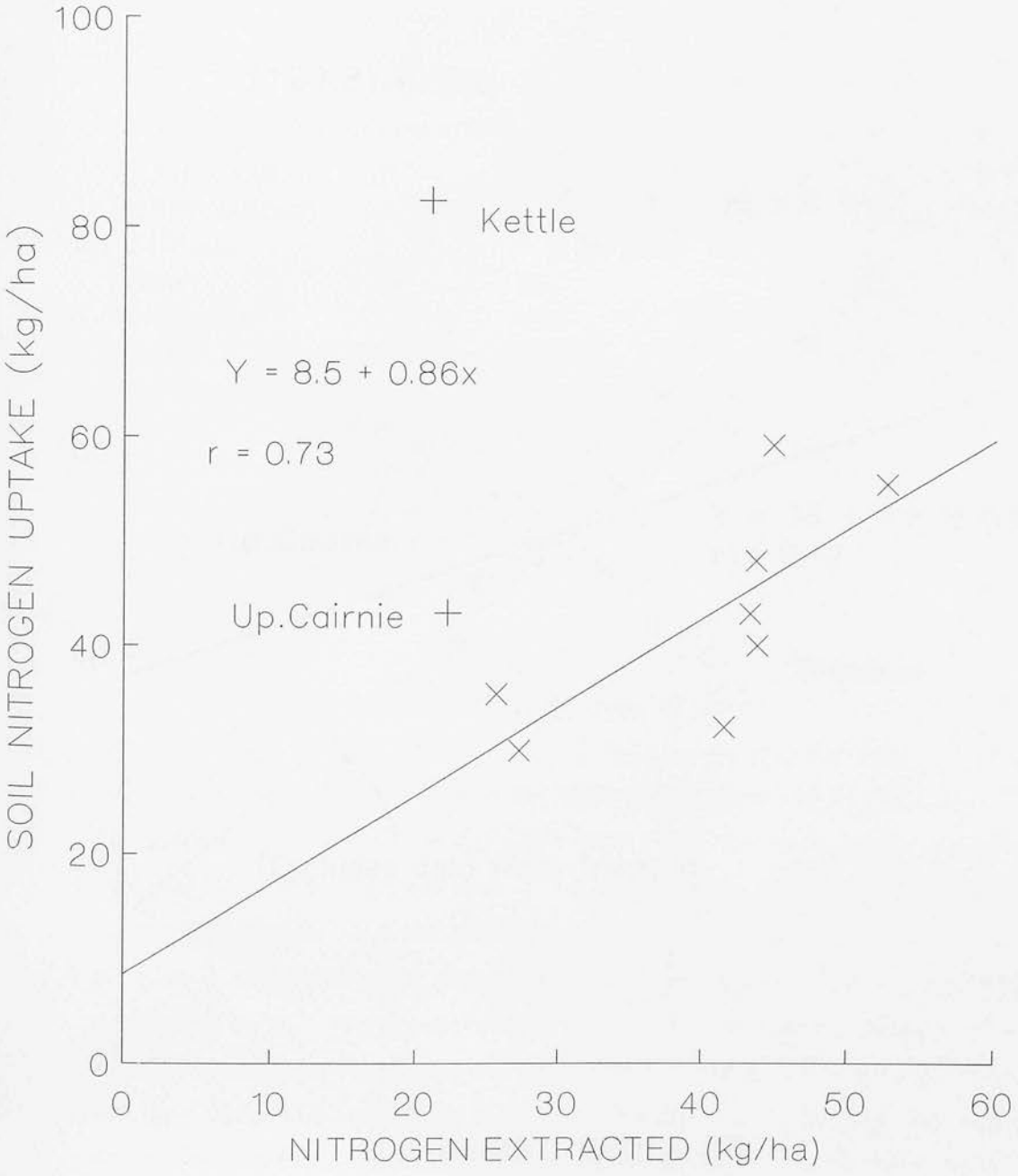


Figure 7.4. Relationship between nitrogen extracted by the Whitehead method and soil nitrogen uptake in the grain only. (Relationship excludes data from Upper Cairnie and Kettle).

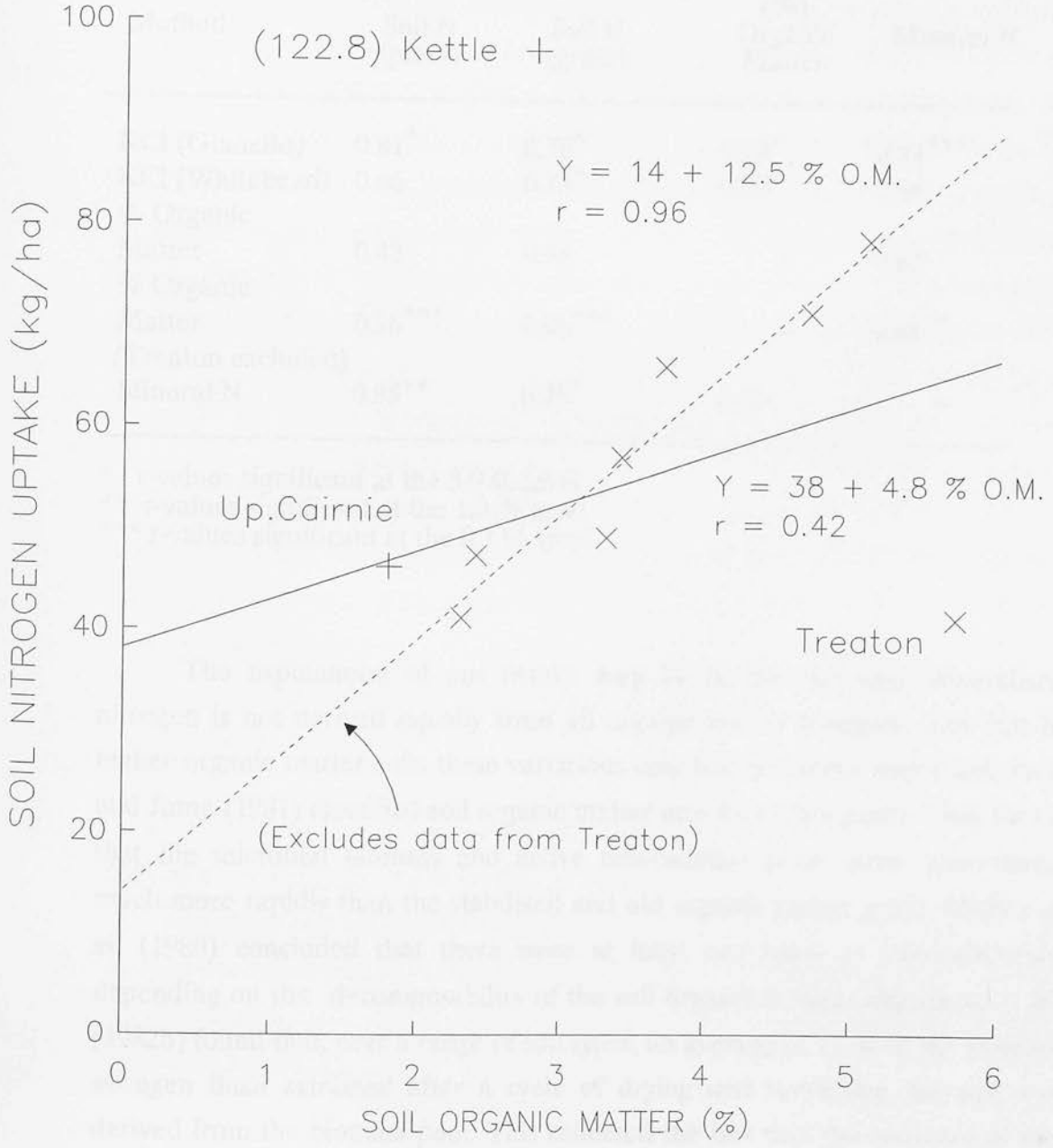


Figure 7.5. Relationship between soil organic matter and soil nitrogen uptake in above ground plant tissue. (Relationship excludes data from Upper Cairnie and Kettle).

Table 7.3: Correlation coefficients for relationships between the measurements of soil nitrogen in the plants and estimates of potentially available soil nitrogen.

	Correlation coefficient (r)			
	Measure of N in plants			
Method	Soil N (plant)	Soil N (grain)	(%) Organic Matter	Mineral N
KCl (Gianello)	0.81*	0.78*	0.80*	0.93***
KCl (Whitehead)	0.66	0.73*	0.70*	0.66
% Organic Matter	0.42	0.44	--	0.63
% Organic Matter (Treaton excluded)	0.96***	0.96***	--	0.84**
Mineral N	0.85**	0.75*	0.63	--

* r-values significant at the 5.0 % level
** r-values significant at the 1.0 % level
*** r-values significant at the 0.1 % level.

The explanation of our results may lie in the fact that mineralised nitrogen is not derived equally from all organic matter fractions, and that in higher organic matter soils these variations may become more important. Paul and Juma (1981) classified soil organic matter into four main pools. They found that the microbial biomass and active non-biomass pools were mineralised much more rapidly than the stabilised and old organic matter pools. Molina *et al.* (1980) concluded that there were at least two rates of mineralisation, depending on the decomposability of the soil organic matter. Marumoto *et al.* (1982b) found that, over a range of soil types, an average of 77 % of the mineral nitrogen flush extracted after a cycle of drying and re-wetting the soil was derived from the biomass pool. This reflected the fact that the turnover of the biomass was five times faster than other fractions of soil organic matter (Amato

and Ladd, 1980; Marumoto *et al.*, 1982a). However, Paul and Juma (1981) found that during a 12-week incubation of a loam soil the biomass, active non-biomass and stabilised organic matter pools contributed equally to the total nitrogen mineralised. The faster turnovers of the biomass and active non-biomass pools were offset by the fact that they only represented approximately 5 % and 8 %, respectively, of the total soil nitrogen.

Whereas these pools contribute the bulk of the mineralised nitrogen, a significant quantity can also be derived from the stabilised organic matter pool (Juma and Paul, 1984). This pool is much larger than the more active pools and therefore it may be that contributions of mineralised nitrogen from the stabilised organic matter pool are more accurately reflected by the overall size of the soil organic matter pool. When both the KCl-extracted nitrogen (which reflects the size of the biologically more active pools of the soil organic matter (Jenkinson, 1968)) and total soil organic matter were taken into account, a much better correlation was obtained with soil nitrogen uptake in the plant (Figure 7.6). This was achieved using multiple stepwise regression analysis which showed that, after taking into account the KCl factor, it was the organic matter content of the soil which was the most significant factor. By considering both of these factors in a multiple regression equation 81 % of the variation in soil nitrogen uptake in the plant was accounted for, and the Treaton site was now no longer an outlier.

7.2.3: Soil pH and texture

Other soil factors such as pH and texture were also considered, but these did not significantly improve predictive correlations either individually or jointly with any other factors. This may be at least partly due to the fact that the soils studied were confined to relatively narrow range of pH values ranging from 5.7 - 6.7 and where most soil textures were either sandy loam or sandy clay loam (Tables 3.1 and 3.3).

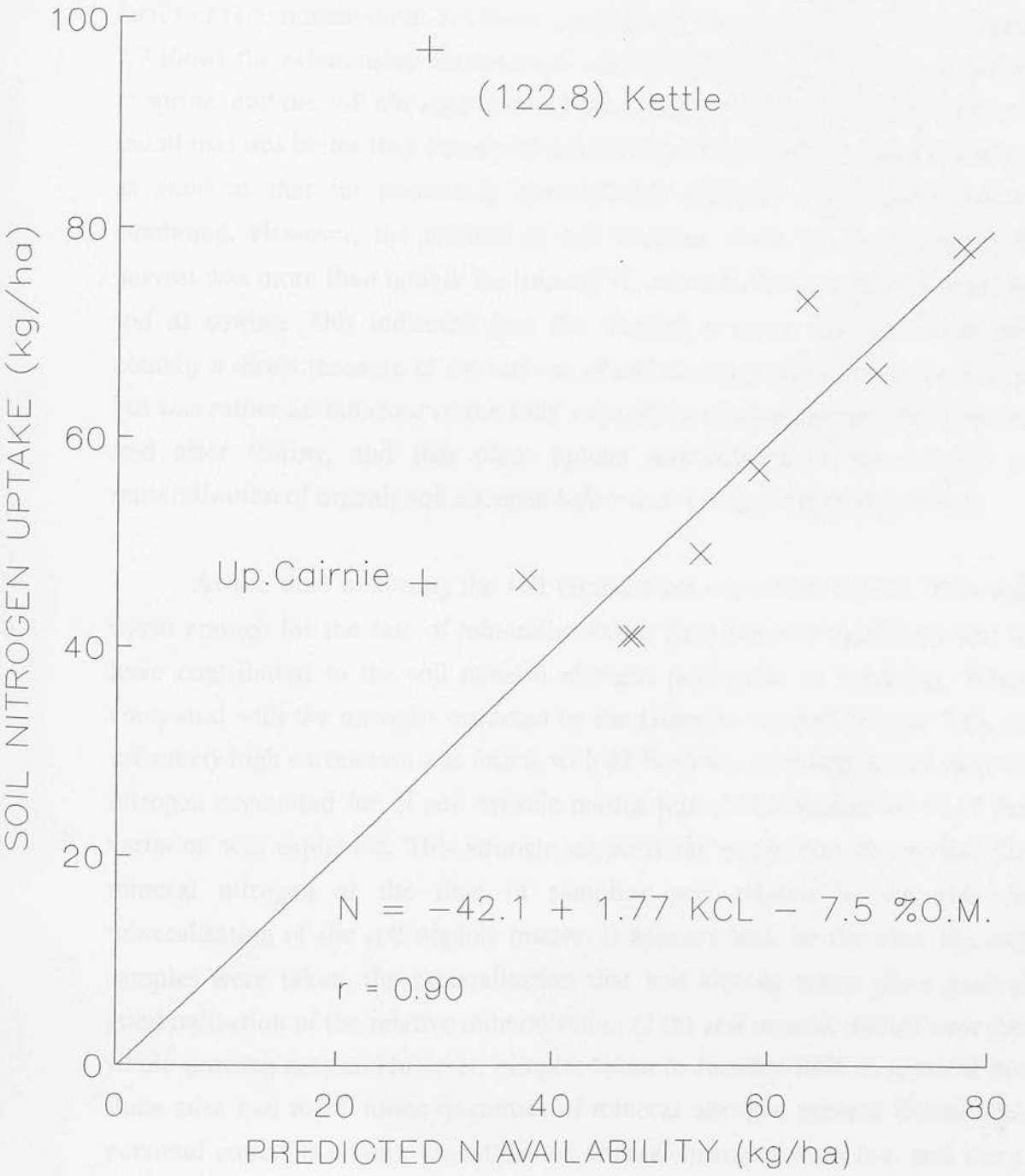


Figure 7.6. Relationship between prediction of soil nitrogen availability (based on both soil organic matter and nitrogen extracted by the Gianello and Bremner method) and soil nitrogen uptake in above ground plant tissue. (Relationship excludes data from Upper Cairnie and Kettle).

7.2.4: Mineral nitrogen in the soil

In Western Europe, fertiliser recommendations are generally based either wholly or partly on the amount of soil mineral nitrogen present in early spring (Greenwood, 1986). In Scotland, however, with generally shallow soils and a cold wet climate, quantities of mineral nitrogen in the spring are low and fertiliser recommendations are based on previous cropping (SAC, 1985). Figure 7.7 shows the relationship between soil mineral nitrogen, at the time of sowing in spring, and the soil nitrogen uptake in the plant. A very good correlation was found that was better than those with potentially mineralisable nitrogen, but not as good as that for potentially mineralisable nitrogen and organic matter combined. However, the amount of soil nitrogen taken up in the plants at harvest was more than double the amount of mineral nitrogen measured in the soil at sowing. This indicated that the mineral nitrogen measured was not actually a direct measure of the amount of soil nitrogen taken up by the plants, but was rather an indicator of the soils' capacity to release nitrogen both before and after sowing, and that plant uptake was related to the amount of mineralisation of organic soil nitrogen *before and during* the growing season.

At the time of sowing the soil temperature was about 6-7 ^{o}C. This was warm enough for the rate of mineralisation to have become significant and to have contributed to the soil mineral nitrogen pool prior to sampling. When compared with the nitrogen extracted by the Gianello method (Figure 7.8), an extremely high correlation was found, with 87 % of the variation in soil mineral nitrogen accounted for. If soil organic matter was also included, 96 % of the variation was explained. This strongly supports the suggestion above that the mineral nitrogen at the time of sampling was related to the rate of mineralisation of the soil organic matter. It appears that, by the time the soil samples were taken, the mineralisation that had already taken place gave a good indication of the relative mineralisation of the soil organic matter over the whole growing season. However, samples taken in January 1991 at some of the same sites had much lower quantities of mineral nitrogen present (Stockdale, personal communication). Quantities of mineral nitrogen were low and there was a poor correlation with nitrogen extracted by the Gianello method. This

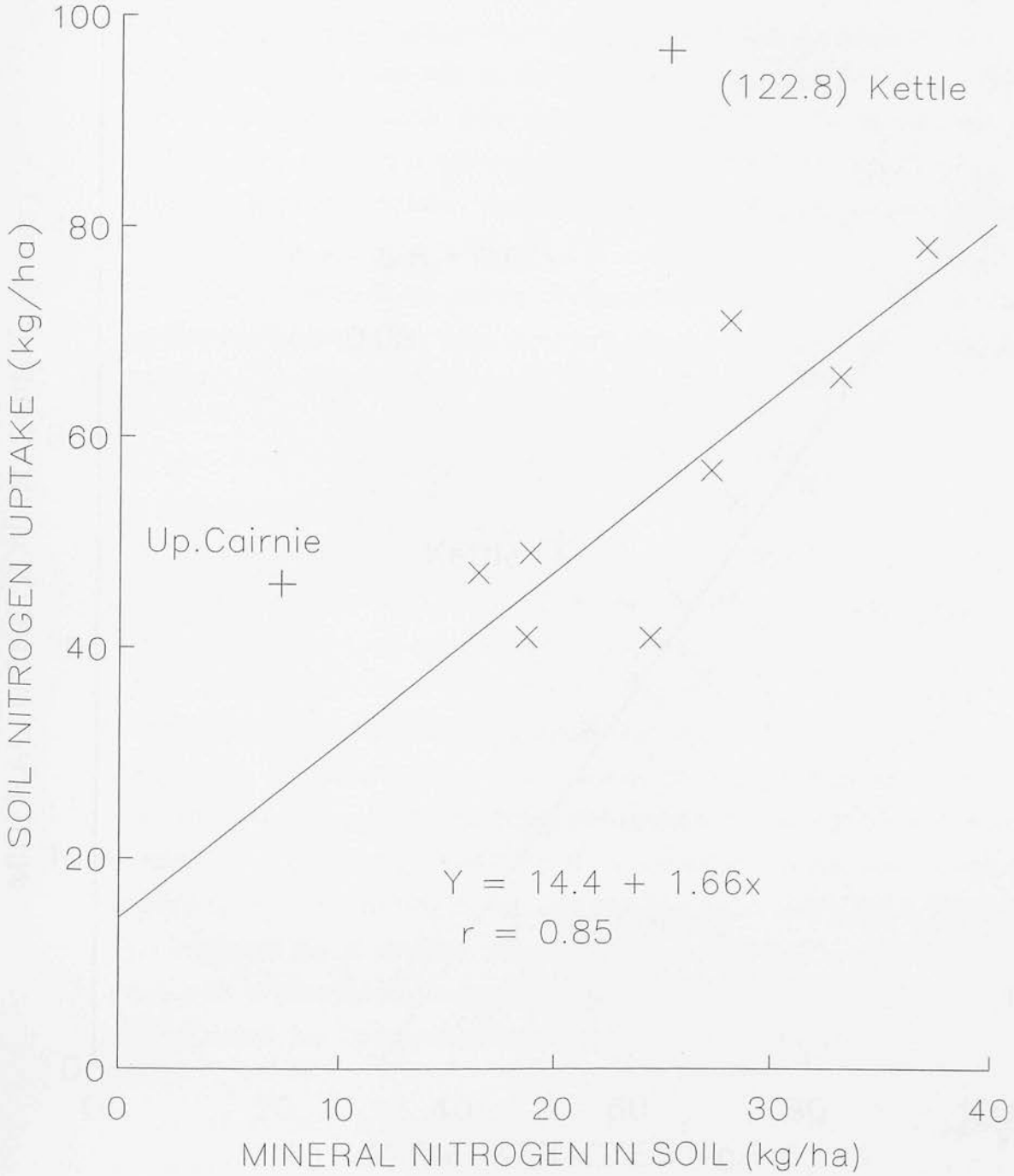


Figure 7.7. Relationship between mineral nitrogen in the soil prior to sowing and soil nitrogen uptake in above ground plant tissue. (Relationship excludes data from Upper Cairnie and Kettle).

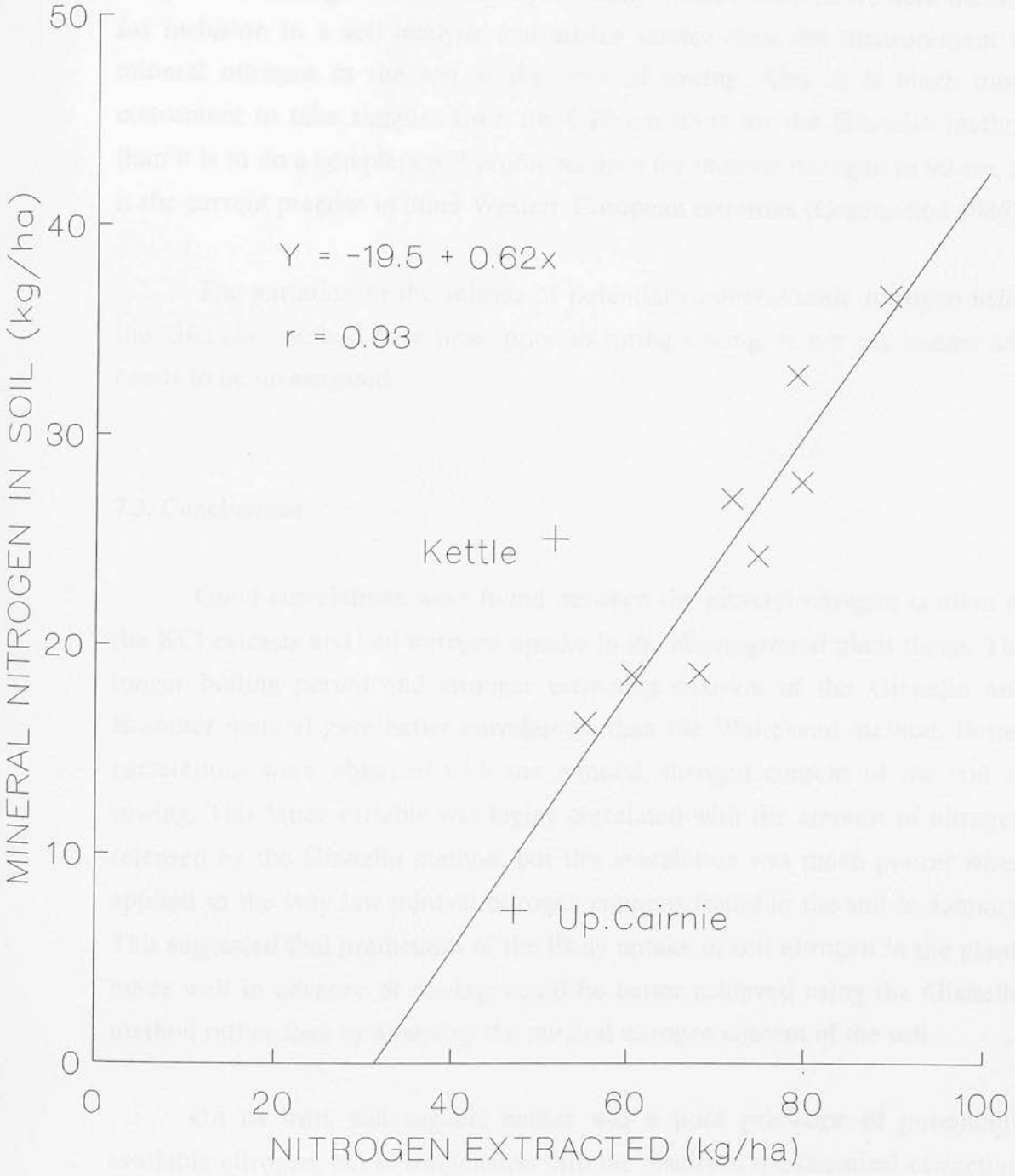


Figure 7.8. Relationship between nitrogen extracted by the Gianello and Bremner method and mineral nitrogen in the soil prior to sowing. (Relationship excludes data from Upper Cairnie and Kettle).

indicated that early sampling and analysis of soil mineral nitrogen content was unlikely to be a good predictor of the uptake of soil nitrogen in the plants at harvest.

The fact that soil sampling and extraction with hot KCl could be carried out prior to sowing means that it is potentially a much more convenient method for inclusion in a soil analysis and advice service than the measurement of mineral nitrogen in the soil at the time of sowing. Also, it is much more convenient to take samples from the 0-20 cm layer for the Gianello method than it is to do a complete soil profile analysis for mineral nitrogen to 90 cm, as is the current practice in other Western European countries (Greenwood 1986).

The variation in the release of potentially mineralisable nitrogen using the Gianello method over time, prior to spring sowing, is not yet known and needs to be investigated.

7.3. Conclusions

Good correlations were found between the mineral nitrogen content of the KCl extracts and soil nitrogen uptake in the above-ground plant tissue. The longer boiling period and stronger extracting solution of the Gianello and Bremner method gave better correlations than the Whitehead method. Better correlations were obtained with the mineral nitrogen content of the soil at sowing. This latter variable was highly correlated with the amount of nitrogen released by the Gianello method, but this correlation was much poorer when applied to the very low mineral nitrogen contents found in the soil in January. This suggested that predictions of the likely uptake of soil nitrogen in the plant, made well in advance of sowing, could be better achieved using the Gianello method rather than by analysing the mineral nitrogen content of the soil.

On its own, soil organic matter was a poor predictor of potentially available nitrogen, but in conjunction with the results of the chemical extraction methods correlations were significantly higher than with any individual method.

The relationships described only applied to N-Index zero soils following a cereal, and did not hold for soils with different plant residues. Further work will be required to establish whether comparable, but quantitatively different relationships can be established for different categories of soils.

8: OVERALL CONCLUSIONS

The aims of this project were to study the effect of nitrogen, as affected by fertiliser nitrogen management and soil nitrogen supply, on the yield and grain nitrogen concentration of spring barley grown for malting.

The form of applied fertiliser nitrogen did not significantly effect the concentration of nitrogen in the grain, with the exception of the two sites in 1989 when concentrations were higher in the calcium nitrate treatments (Section 4.1). It appeared that there was a greater recovery of the more mobile nitrate fertiliser in those treatments, which, in conjunction with reduced grain filling due to the high moisture stress at these sites, resulted in higher grain nitrogen concentrations. At lower fertiliser rates, grain yields were generally improved at most sites when the fertiliser was applied as calcium nitrate. However, at fertiliser rates nearer recommended levels, there was little difference in yield between the fertiliser forms.

Split or late applications of 120 kg N/ha fertiliser nitrogen only improved yields when applied as calcium nitrate, and then only when the early applications were followed by heavy rain, which increased the risk of leaching losses (Section 4.1). In 1989, split applications at the lower rate of 90 kg N/ha improved yields to the equivalent of those obtained with 120 kg N/ha applied at sowing. There was no increase in grain nitrogen concentrations between split applications and applications of the same rate all applied at sowing. (Section 4.1.3).

At low fertiliser rates, the efficiency of recovery of fertiliser nitrogen (^{15}N) in the plant shoots was greater, when applied as calcium nitrate, than when applied as either ammonium sulphate or ammonium nitrate. The cause of this enhanced recovery of nitrogen applied entirely as nitrate appeared to be the enhanced mobility of the nitrate, compared with the ammonium ion. At higher fertiliser rates, the efficiency of recovery fell in the calcium nitrate treatments, but rose in the ammonium sulphate treatments. Under the dry soil conditions in

1989, recoveries of fertiliser nitrogen significantly increased in all fertiliser treatments (Section 4.2).

Uptake of fertiliser nitrogen was rapid in the calcium nitrate and ammonium nitrate treatments, usually reaching a maximum by anthesis. There was evidence of net losses between anthesis and harvest of up to 26 kg N/ha of fertiliser ^{15}N previously taken up by the crop. This could have been due to gaseous losses from old plant tissue or through translocation to, and subsequent exudation from, plant roots. There was little evidence of such losses in the ammonium sulphate treatments, where plant uptake of fertiliser nitrogen was slower. This could have been the result of lower nitrate concentrations in plant tissues, which appear to be an important factor in determining nitrogen losses from plant tissues. Uptake of fertiliser nitrogen continued for several weeks longer in the ammonium sulphate treatments compared to the other fertiliser treatments, possibly due to the re-mineralisation of previously immobilised $^{15}NH_4$-N (Section 4.5).

The uptake of unlabelled nitrogen (soil N) remained constant over the range of rates and timings of fertiliser application in the calcium nitrate treatments. In the ammonium sulphate treatments, however, there was evidence of increased uptake of unlabelled nitrogen at higher fertiliser rates, at several sites. The fact that this phenomenon was most apparent in the ammonium sulphate treatment fertiliser indicated that the cause was probably 'pool substitution' of ^{15}N-labelled fertiliser with unlabelled soil nitrogen by soil micro-organisms. This would have required the fertiliser and soil nitrogen to be present in the same soil pool, which only occurred at the sites with more moist soil conditions. Therefore there appeared to be little evidence of a real priming effect, i.e. of fertiliser applications increasing the rate of mineralisation of soil organic matter (Section 4.2). The rate of soil nitrogen uptake was less rapid than fertiliser nitrogen uptake, during the period up to anthesis. During this period soil nitrogen uptake was often greater in the ammonium sulphate treatments, which again indicated the probable occurrence of pool substitution of ^{15}N-labelled fertiliser (Section 4.5). Unlike the uptake of fertiliser nitrogen, the uptake of soil nitrogen continued up to harvest in most treatments. This late

uptake occurred despite the fact that the amount of mineral nitrogen in the soil had fallen to pre-fertilisation levels (Section 5). This suggested that, later in the growing season, the net mineralisation of soil organic matter was an important contributor of nitrogen to the crop.

The most significant factor which determined total nitrogen uptake in the crop was the soil on which the barley was grown, rather than any of the fertiliser management treatments studied. Soil nitrogen uptake was significantly more variable between sites than fertiliser nitrogen uptake, despite the similar cropping histories at most sites (Sections 4.1.4 and 4.4). This variation in soil nitrogen uptake appeared to be derived more from differences in the mineralisation of soil organic matter over the growing season at each site, than from differences in the amounts of mineral nitrogen in the soil at sowing, which were low and could not account for the observed differences in soil nitrogen uptake (Section 5).

Calculated gross rates of mineralisation rose during the growing season with increasing soil temperatures. This would explain the continued uptake of soil nitrogen throughout the growing season. There was also some variation between sites which roughly correlated to the organic matter content of the soil (Section 6.2.1). The estimated rates of nitrification were generally high; however, some of these rates may have been overestimated due to disproportionate losses of $^{15}NO_3$-N via denitrification shortly after application. These errors appeared to result from a slow mixing of the fertiliser and soil nitrogen pools. A better method of application, possibly injecting the ^{15}N into the soil, might overcome these problems (Section 6.2.5).

Good correlations were found on all ADAS N-Index zero soils, between soil nitrogen uptake in the plant and values obtained using the KCl extraction techniques for measuring potentially mineralisable nitrogen (Section 7.2.1), but this relationship did not hold for the two soils which were not N-Index zero. When the soil organic matter content of the soil was also taken into account, the correlations were better than using the chemical extractions alone. Correlations between soil mineral nitrogen at sowing and soil nitrogen uptake were high, but

the correlations were much poorer when soil mineral nitrogen values were measured in January. In January, the amount of soil mineral nitrogen was significantly lower than that measured at the time of sowing, suggesting that some mineralisation had already occurred by this time. There was a very high correlation between the uptake estimated using the chemical extraction techniques and the amount of mineral nitrogen at sowing, despite the fact that in the estimation of mineralisable N by chemical extraction initial mineral nitrogen values were excluded. This appeared to confirm the contribution of mineralisation to soil mineral nitrogen levels prior to sowing.

The results suggest that the use of a chemical extraction technique may be useful in predicting the potential uptake of soil nitrogen in a crop under field conditions, at least for N-Index zero soils. As most malting barley would be grown on N-Index zero soils, and yet it is clear from the results presented that in these soils the uptake of soil nitrogen is very important in determining the grain nitrogen content, the technique is potentially of great benefit to farmers to ensure their crop is of malting quality. Further work would need to be carried out over a wider range of soils to validate these results, and also to ascertain whether different relationships could be determined for other groups of soils. More research will also need to be carried out to determine if the relationship will hold for earlier sampling, which would be necessary if the technique was to become widely used to advise farmers on modifications to standard rates of fertiliser application.

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APPENDIX

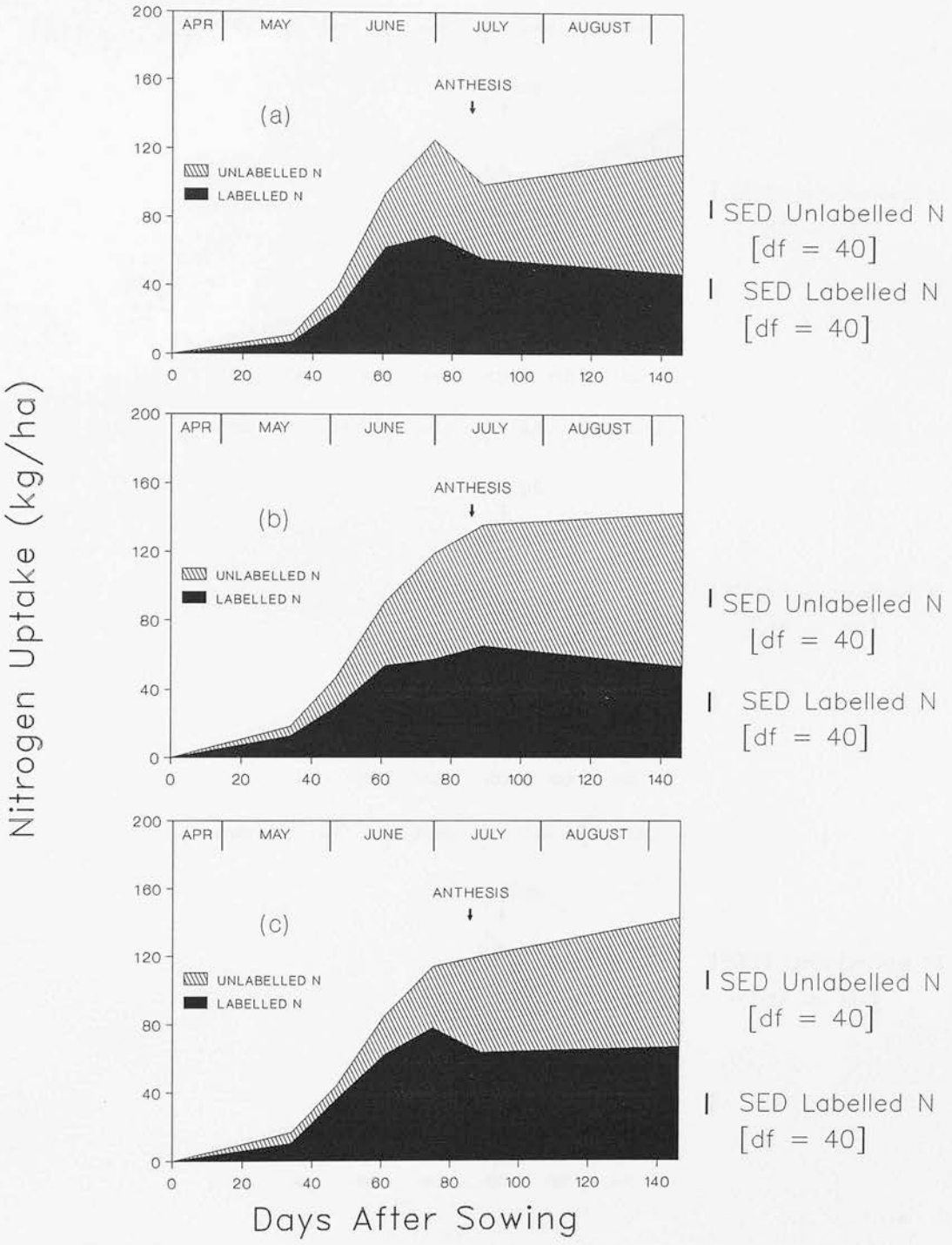

Figure A1. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (Seafield) 1987

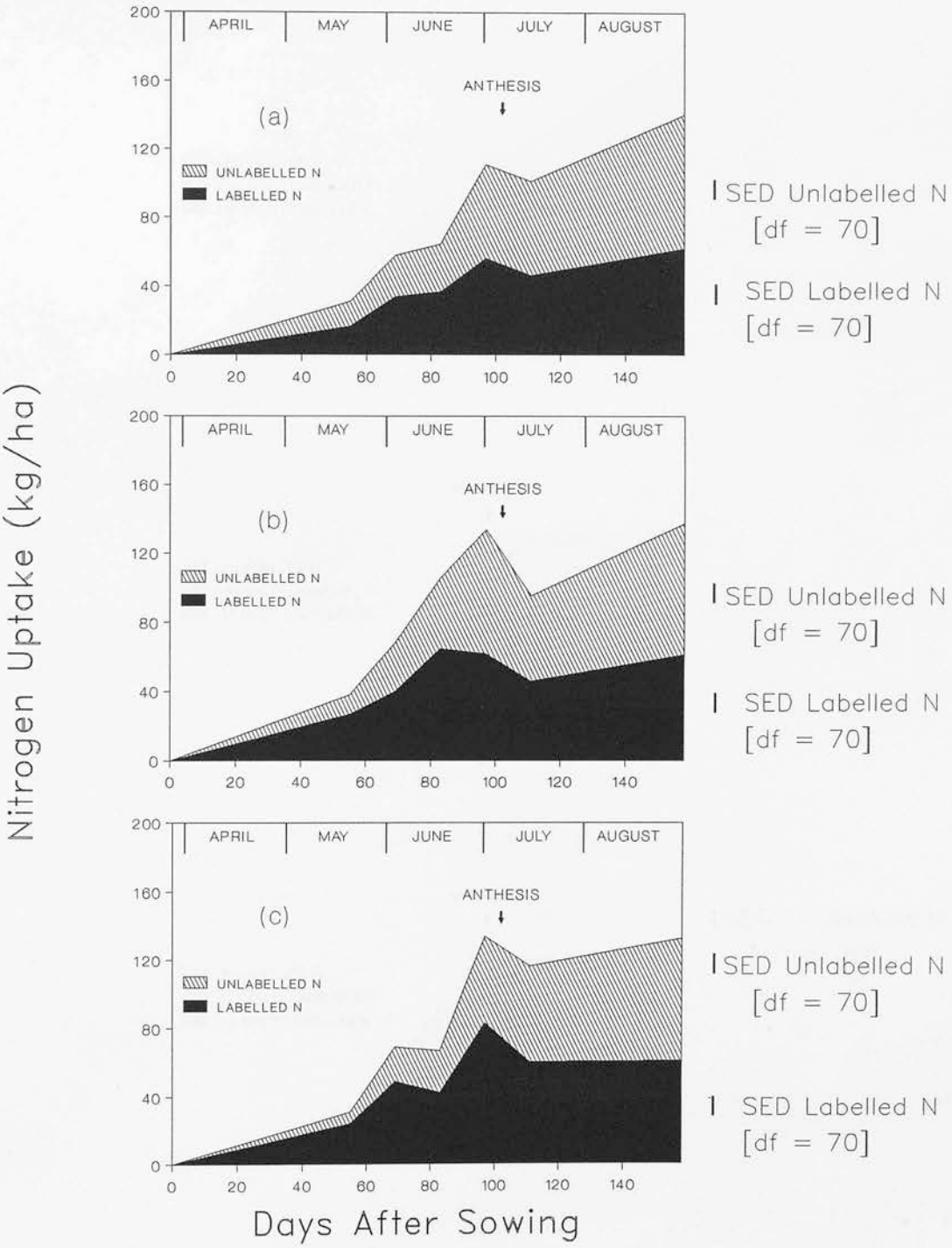

Figure A2. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Lintlaw 1987

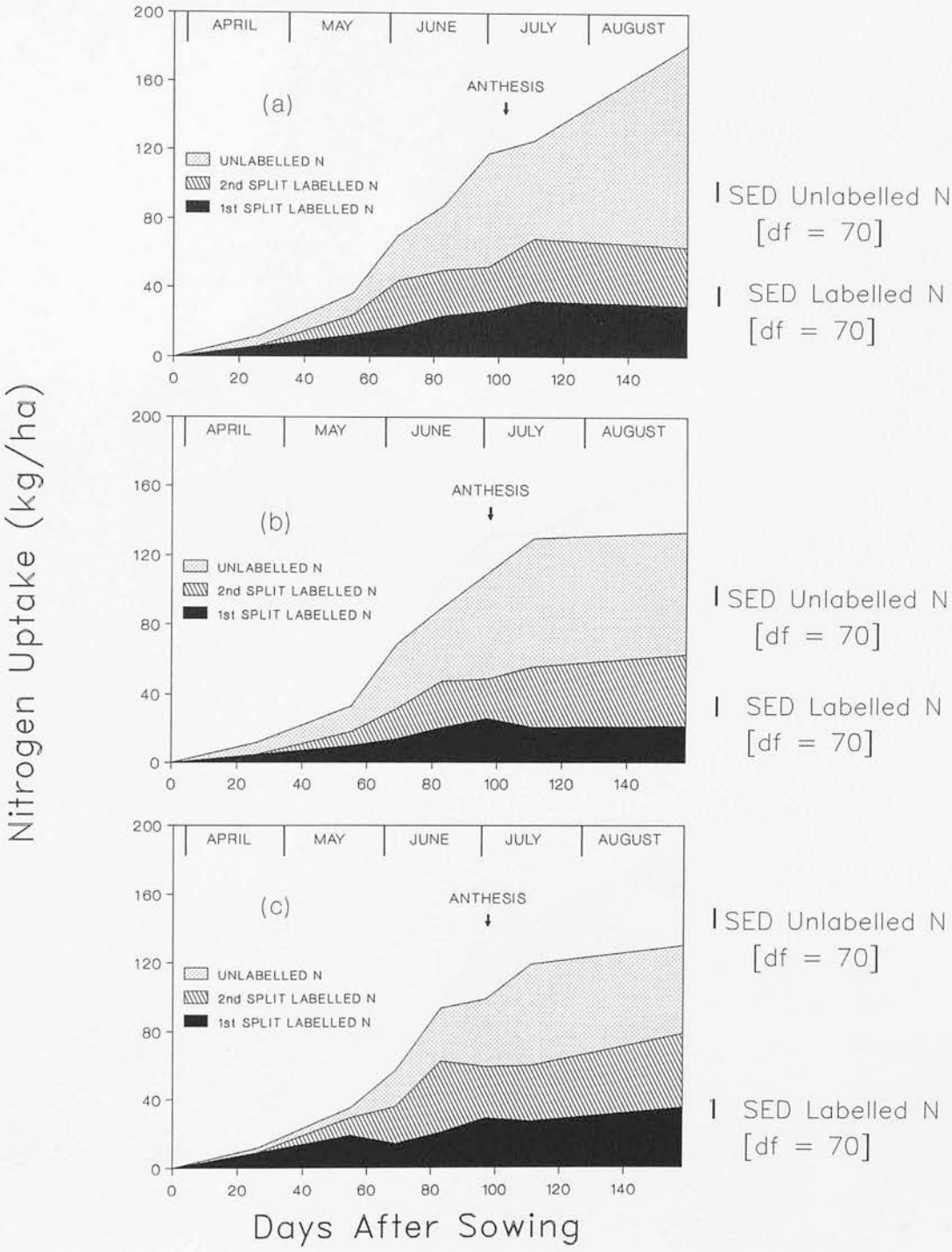

Figure A3. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 60 kg/ha at sowing and 60 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Lintlaw 1987

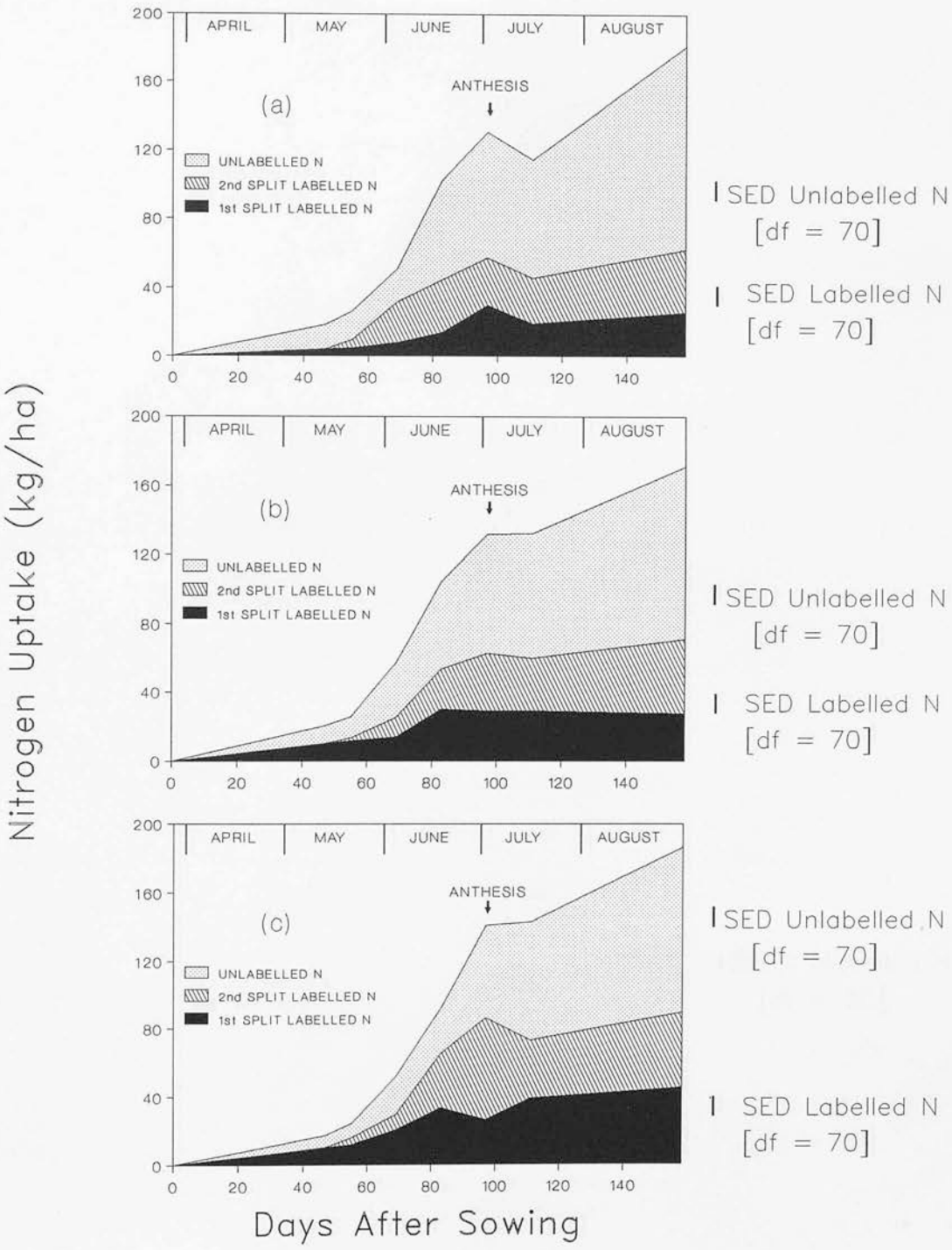

Figure A4. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertilise nitrogen application of 60 kg/ha at sowing and 60 kg/ha at tillering in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Lintlaw 1987

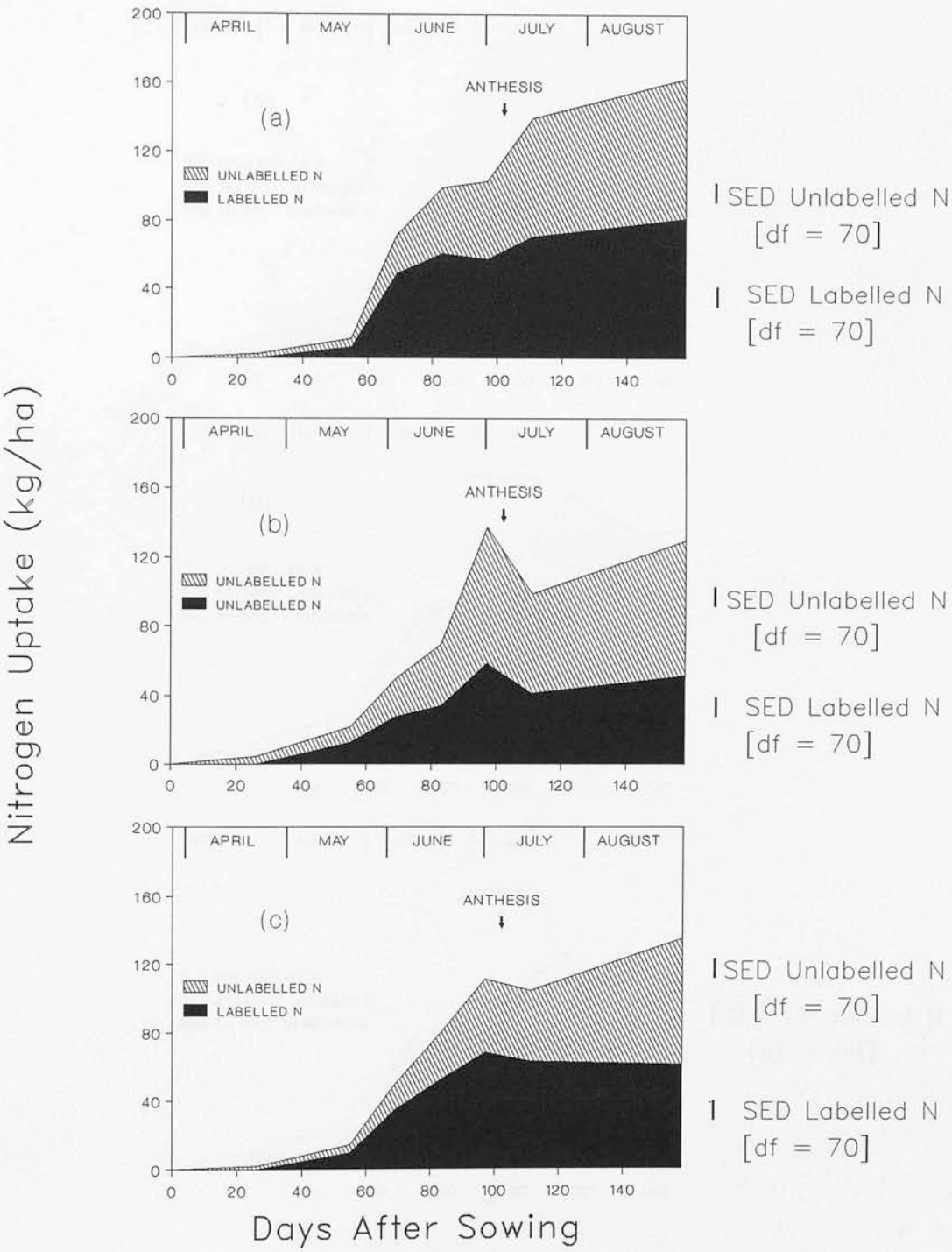

Figure A5. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Lintlaw 1987

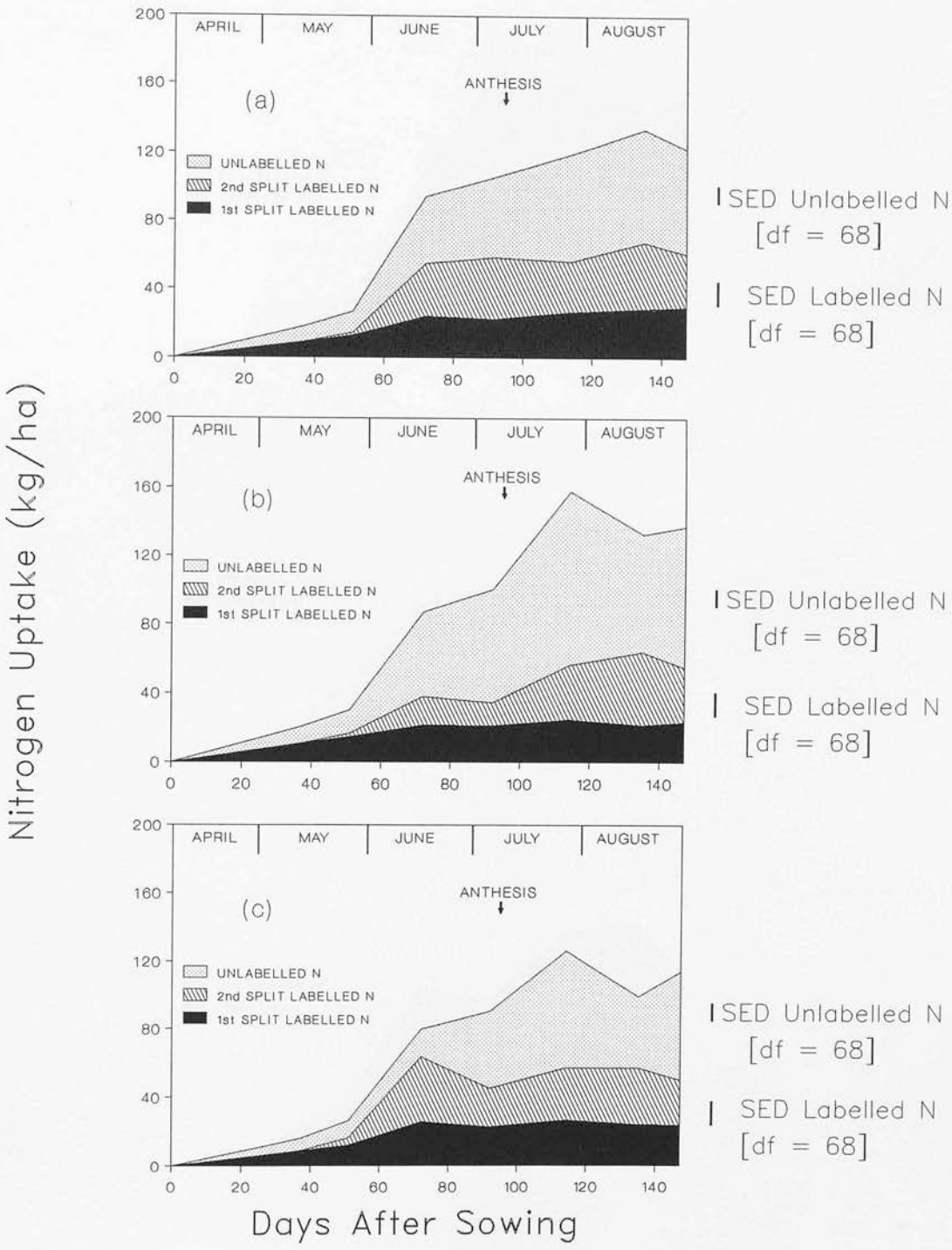

Figure A6. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 60 kg/ha at sowing and 60 kg/ha at tillering in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (Lower Fulford) 1988

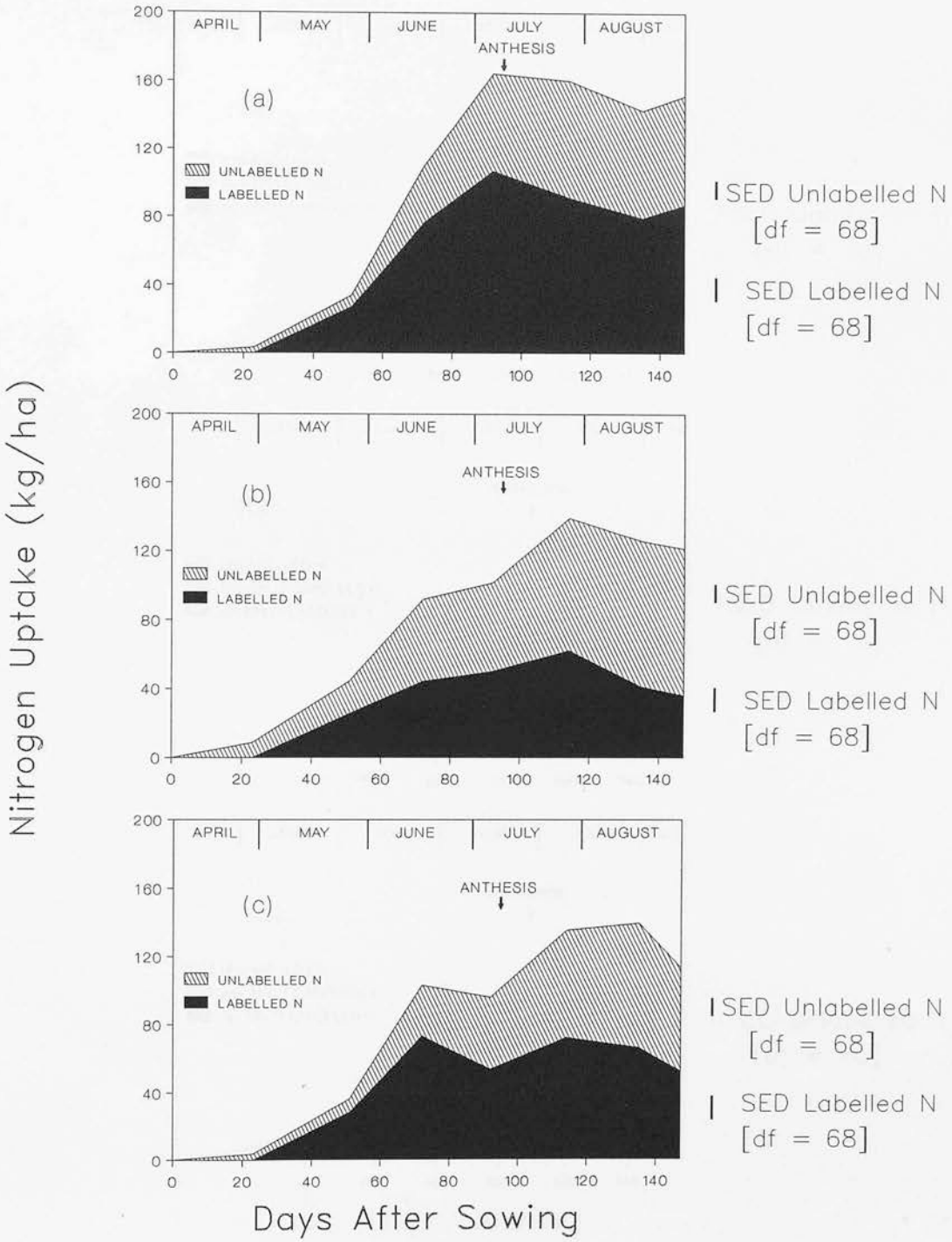

Figure A7. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (Lower Fulford) 1988

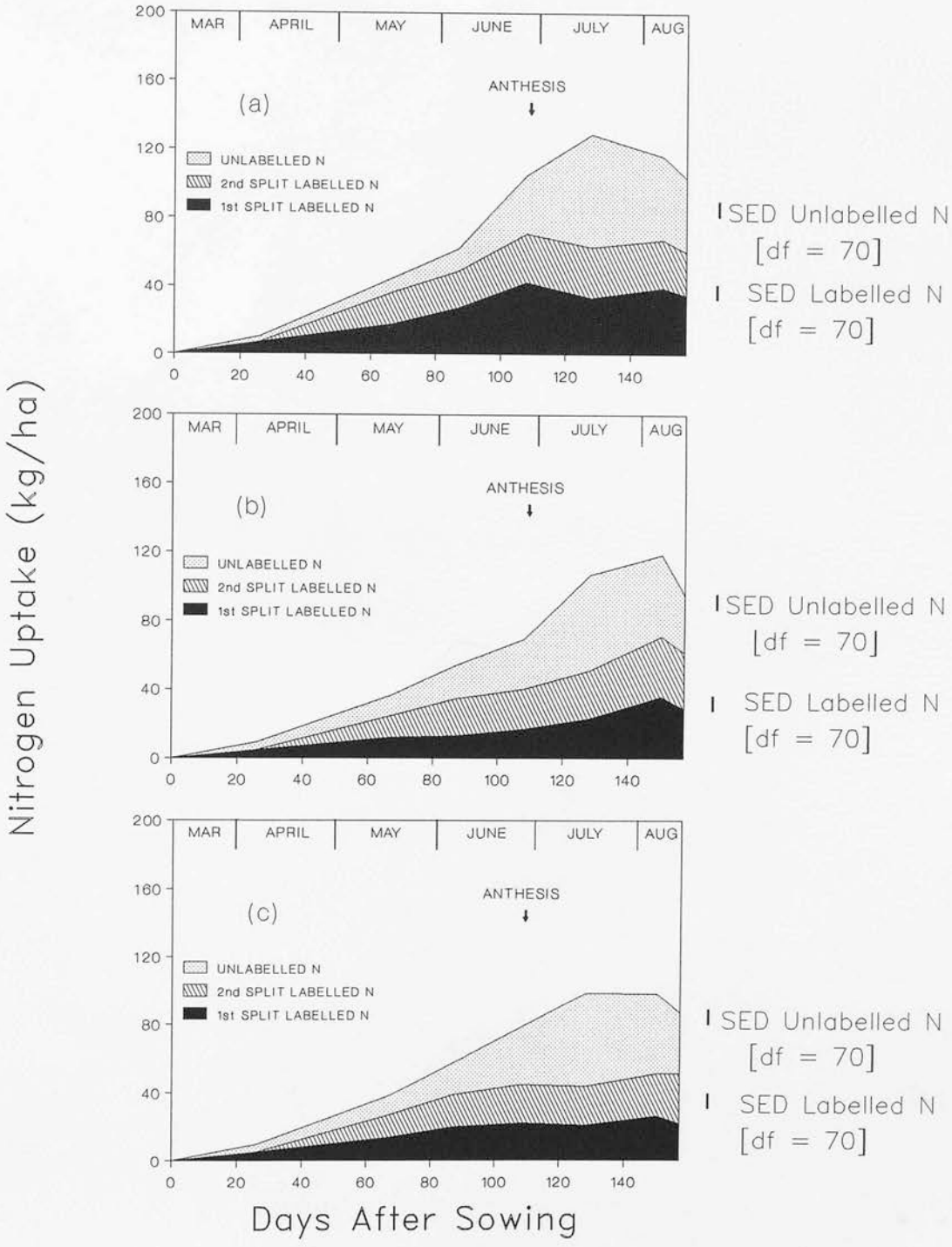

Figure A8. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 60 kg/ha at sowing and 60 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Middlestot 1988

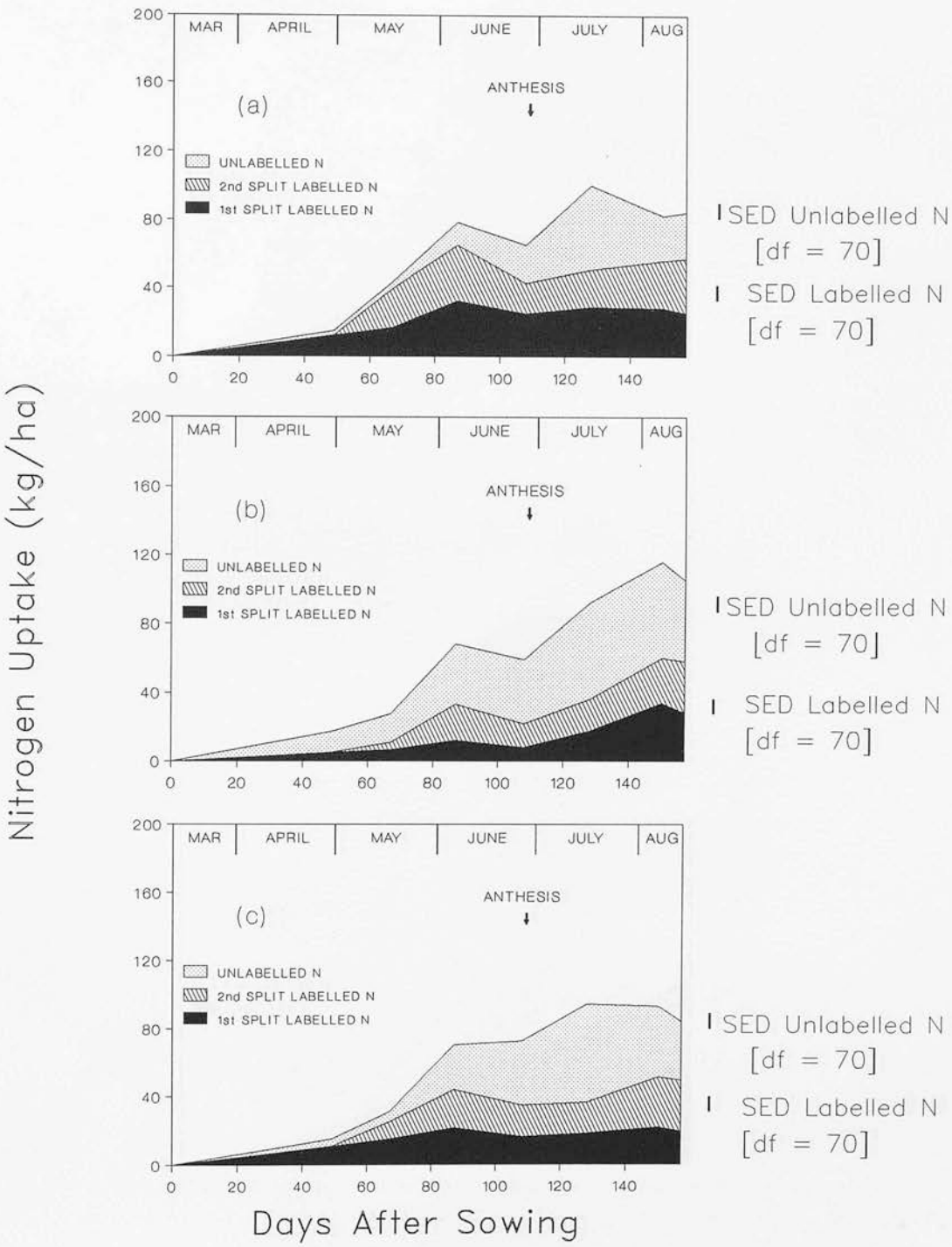

Figure A9. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 60 kg/ha at sowing and 60 kg/ha at tillering in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Middlestot 1988

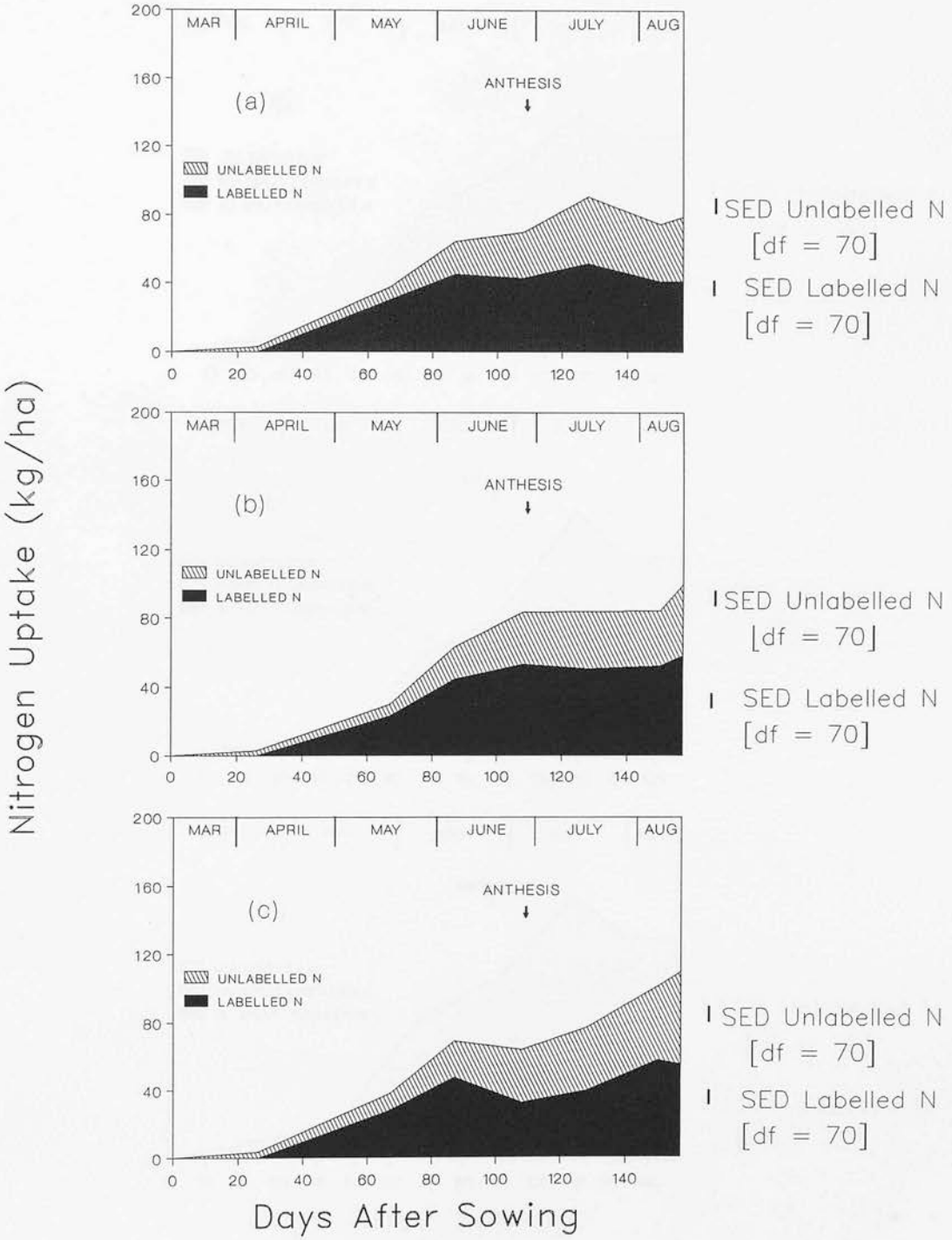

Figure A10. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Middlestot 1988

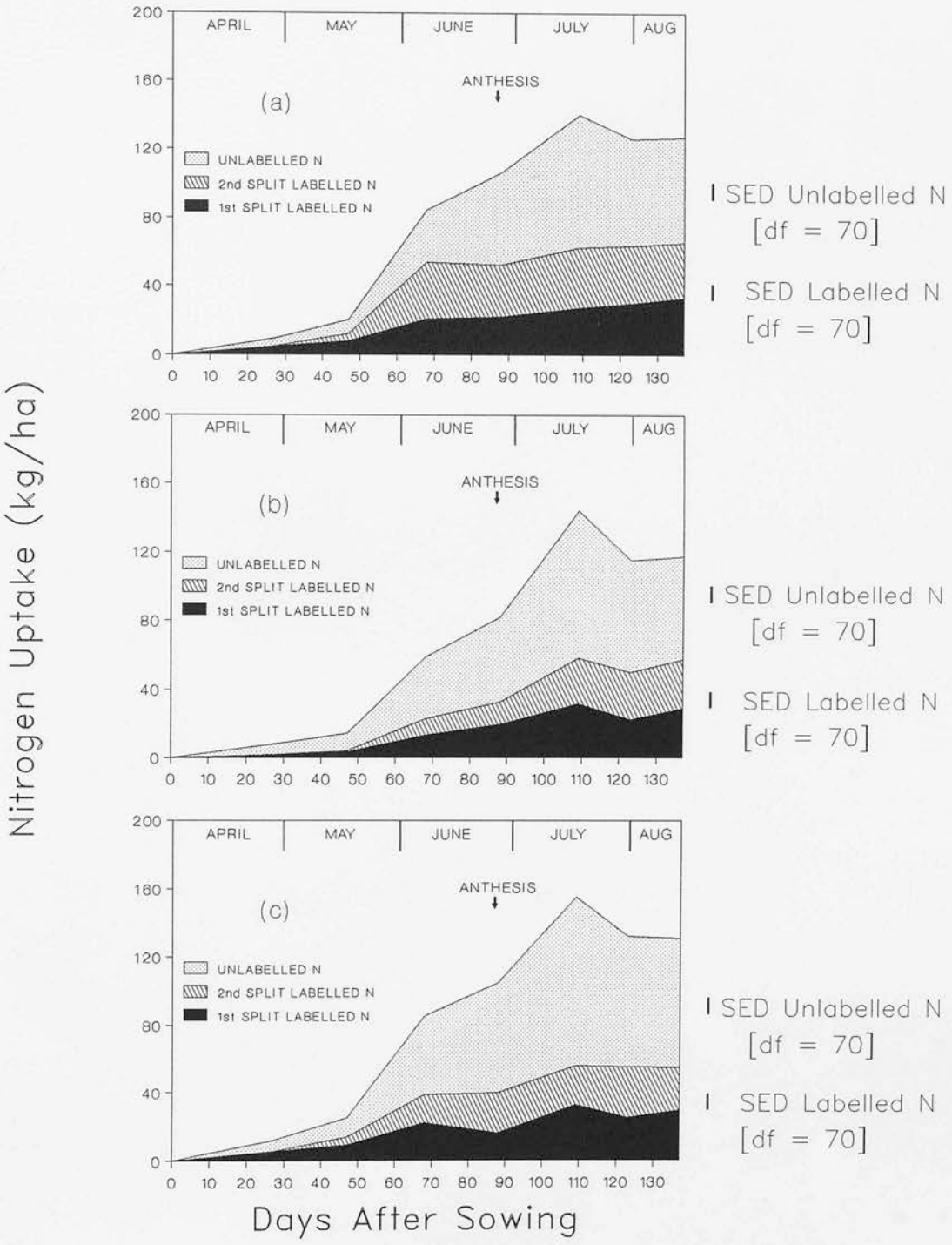

Figure A11. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 45 kg/ha at sowing and 45 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (March Park) 1989

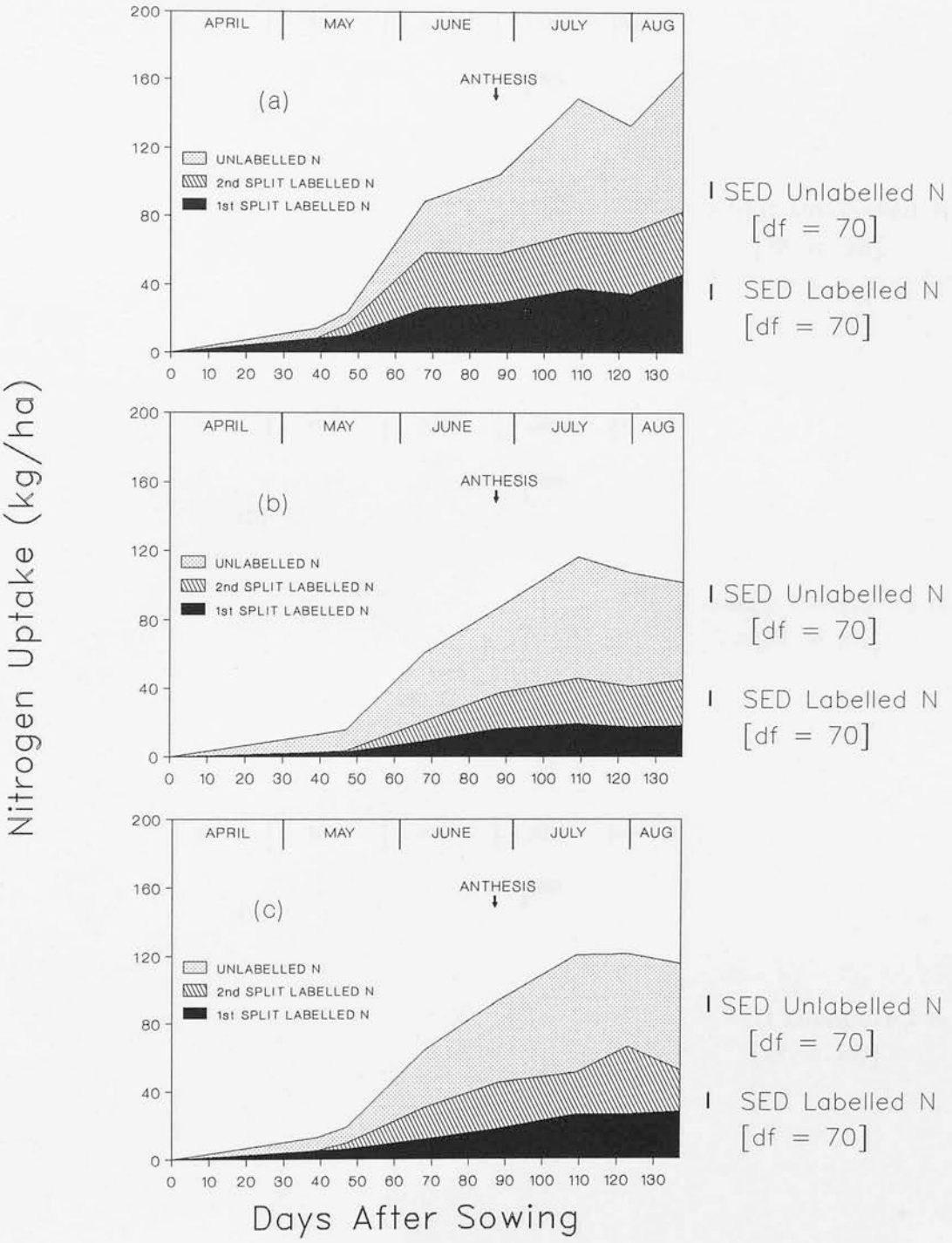

Figure A12. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 45 kg/ha at sowing and 45 kg/ha at tillering in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Bush (March Park) 1989

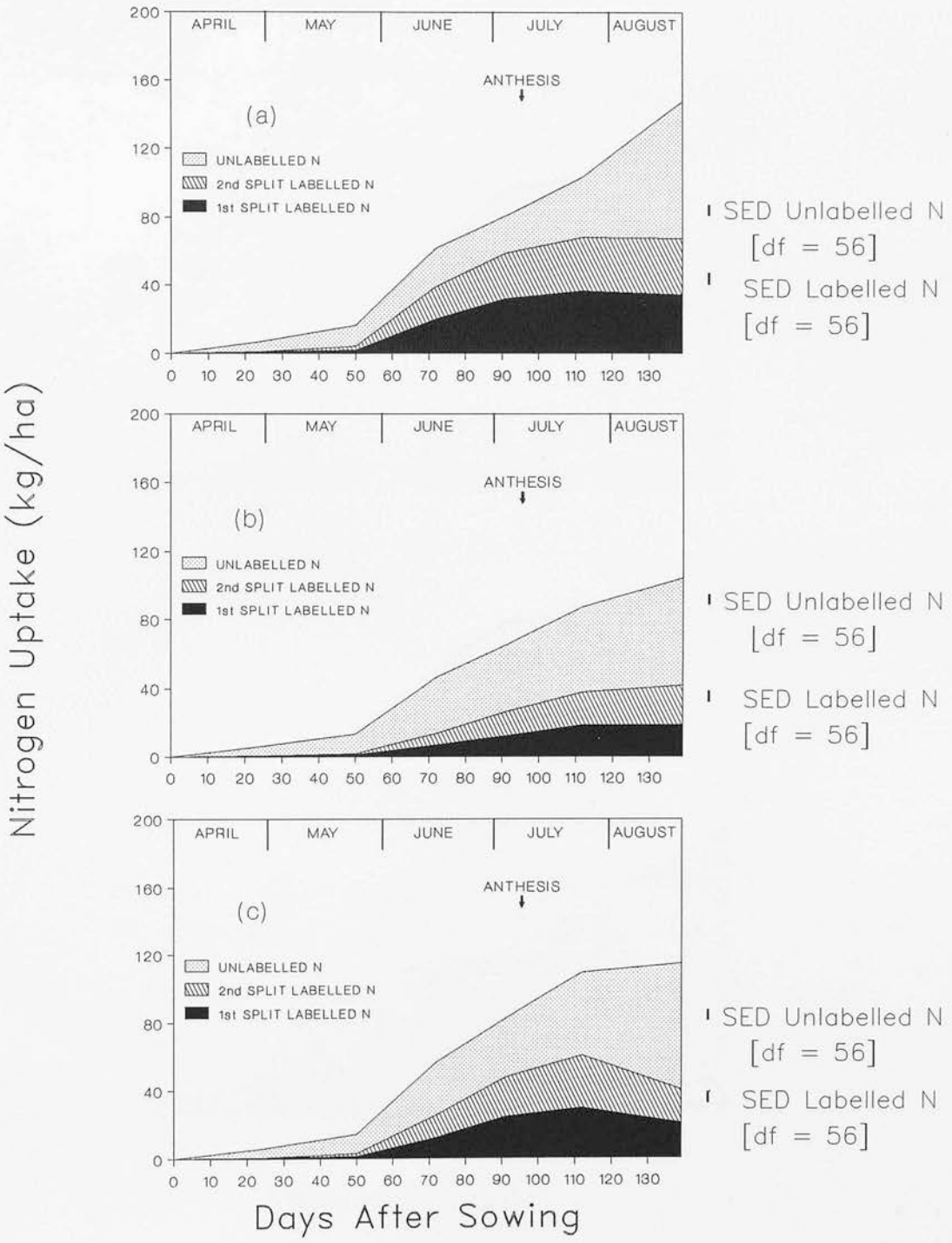

Figure A13. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 45 kg/ha at sowing and 45 kg/ha at emergence in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Upper Cairnie 1989

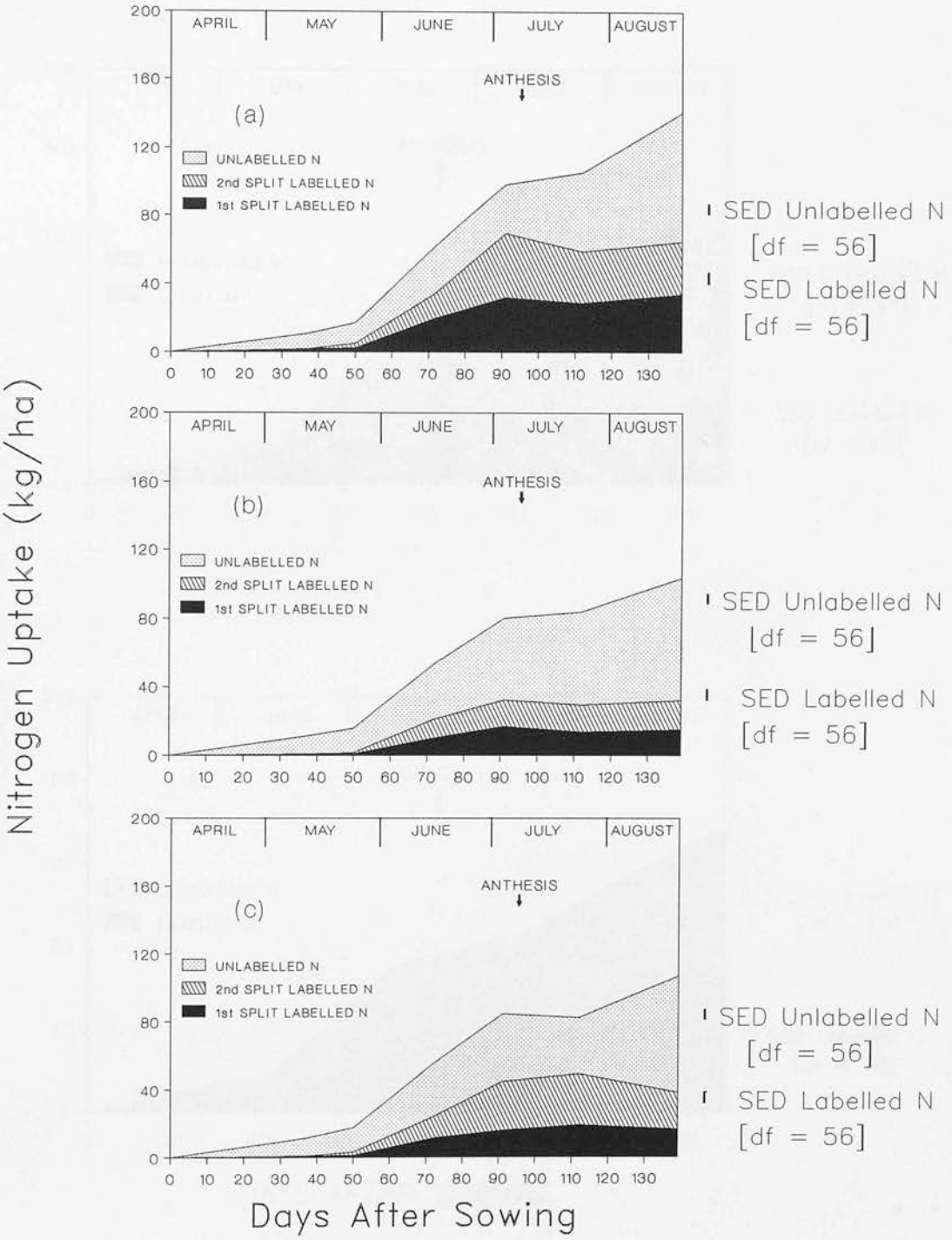

Figure A14. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen application of 45 kg/ha at sowing and 45 kg/ha at tillering in the form of (a) calcium nitrate, (b) ammonium sulphate and (c) ammonium nitrate, Upper Cairnie 1989

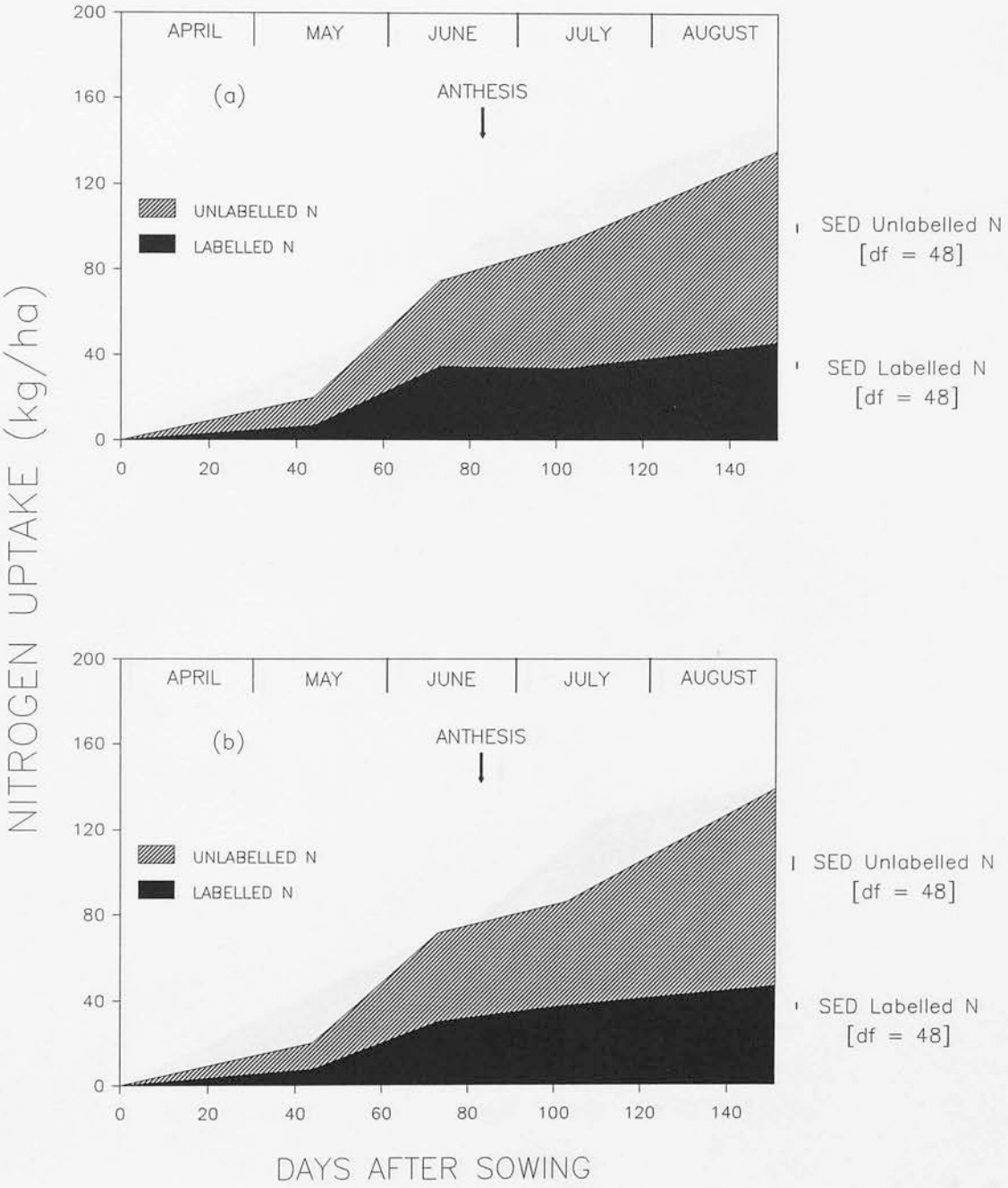

Figure A15. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) ammonium sulphate and (b) ammonium nitrate, Quixwood 1990

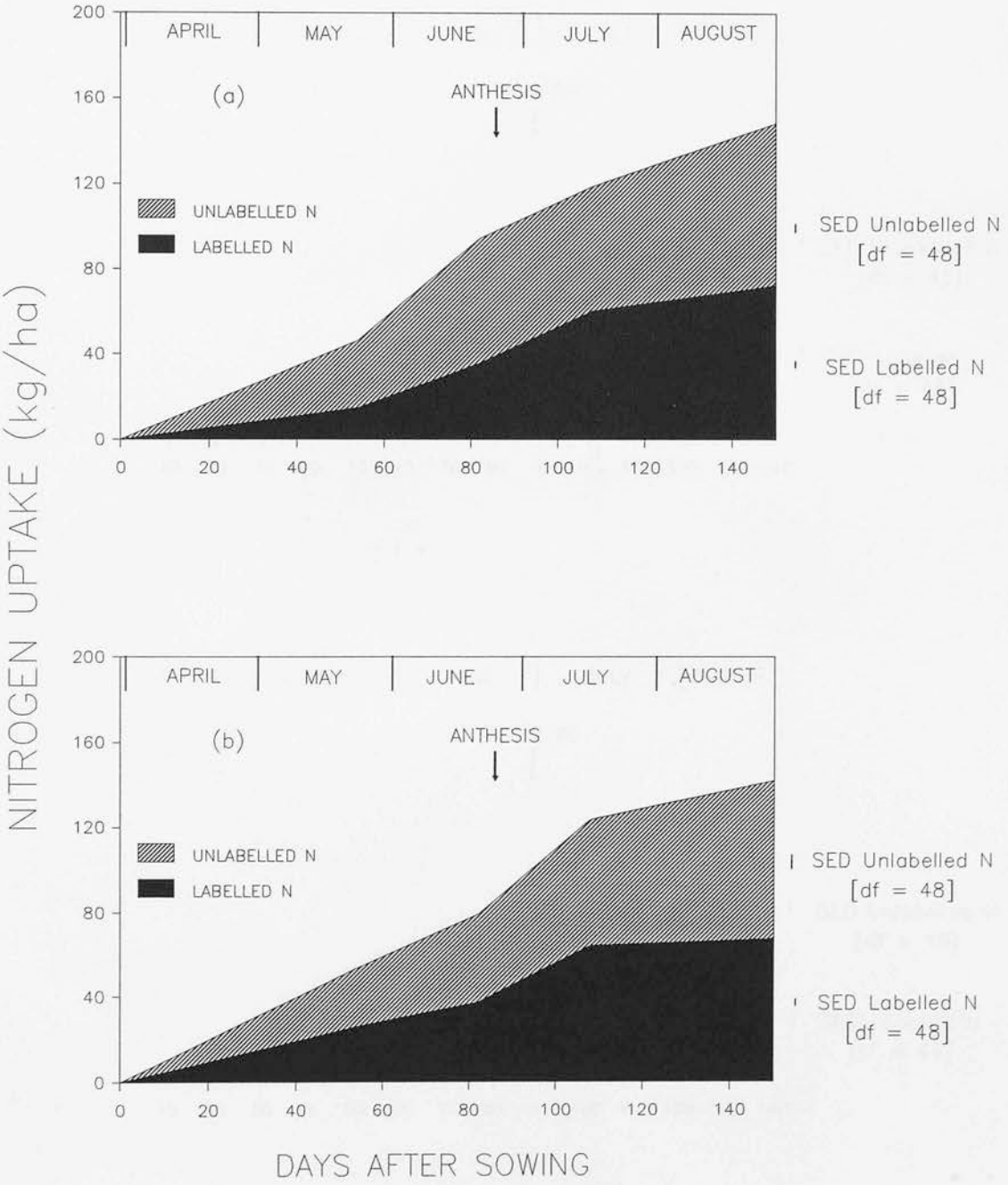

Figure A16. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) ammonium sulphate and (b) ammonium nitrate, Bush (Crofts) 1990

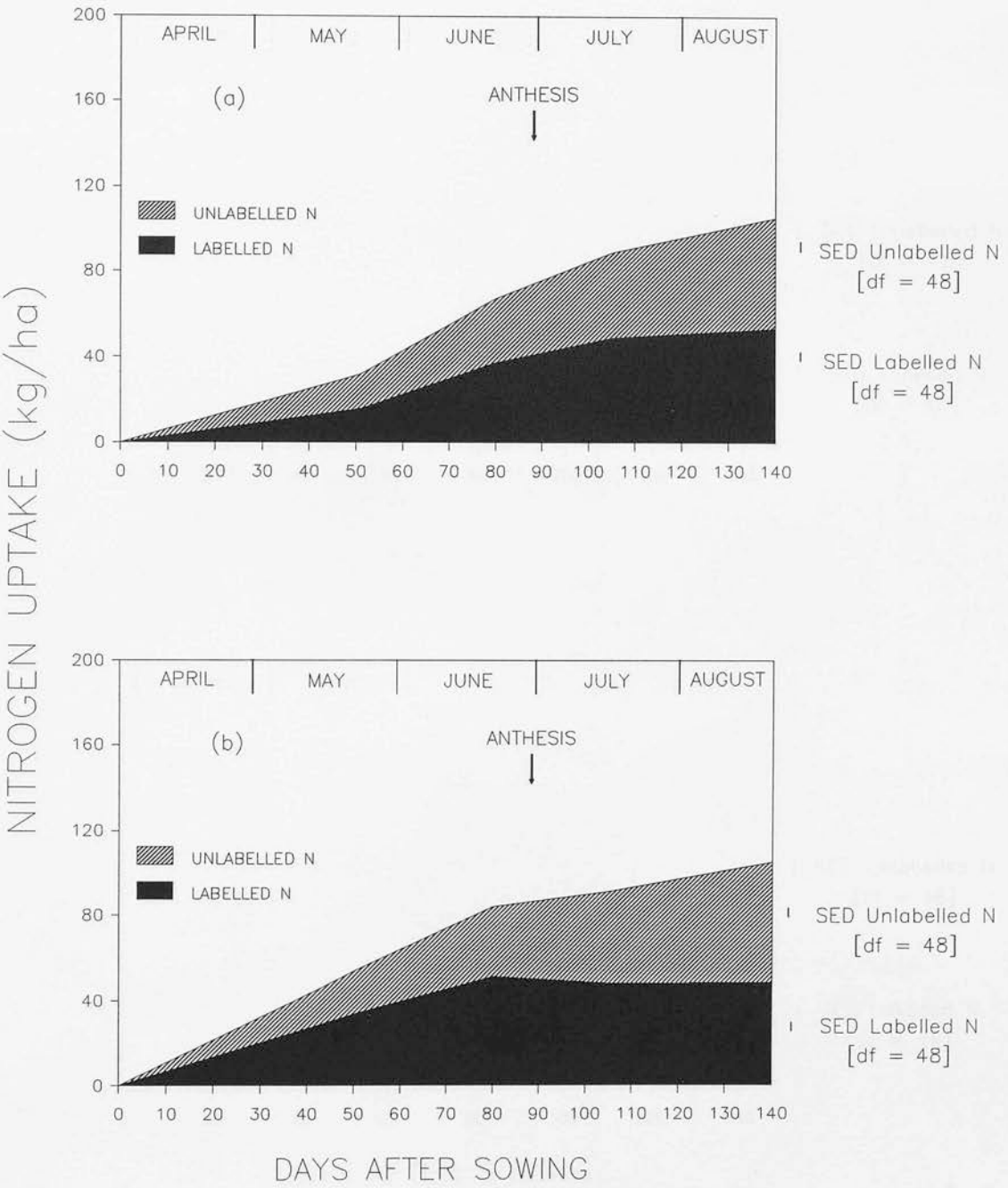

Figure A17. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) ammonium sulphate and (b) ammonium nitrate, Bush (Farmers' Holding) 1990

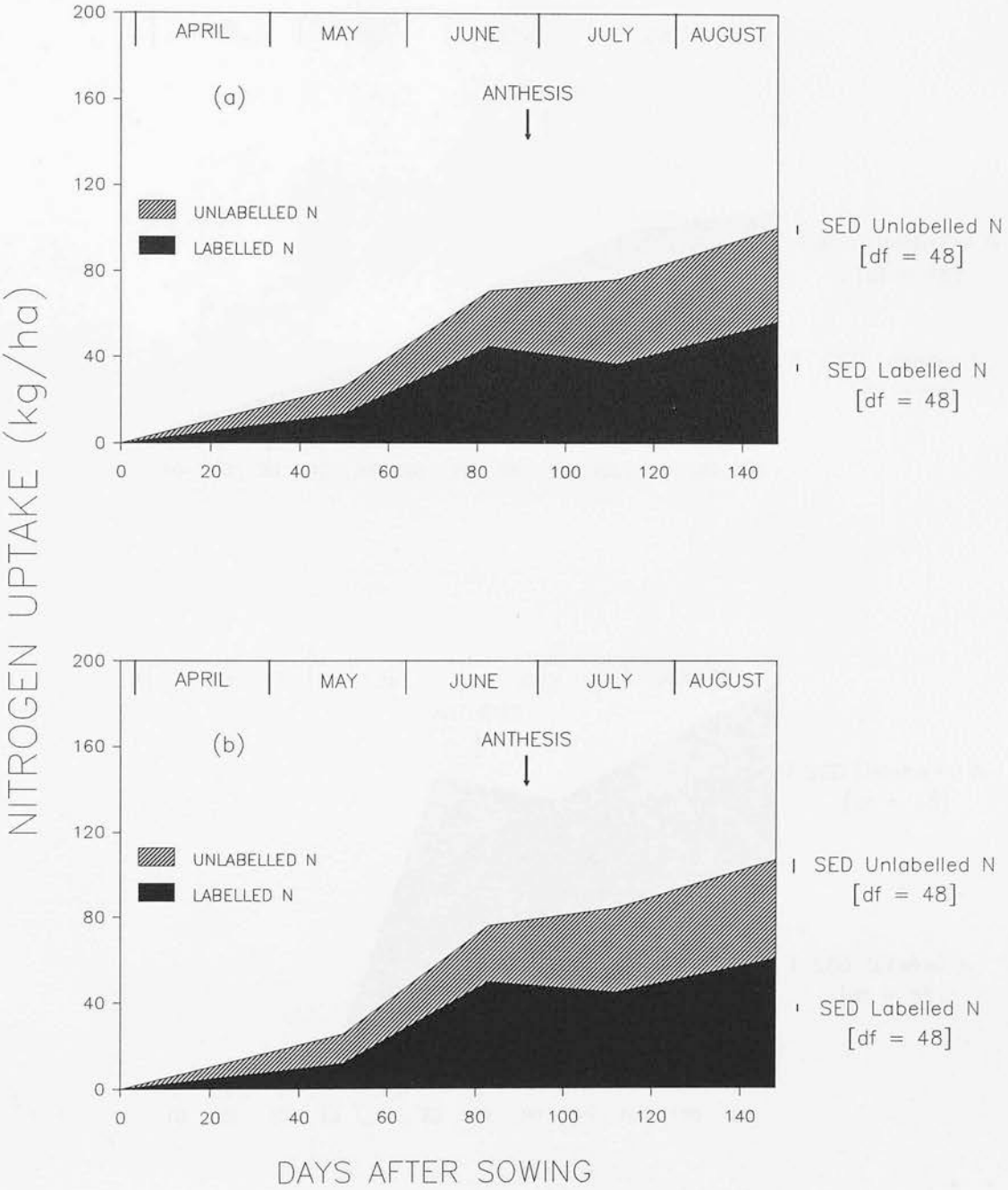

Figure A18. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after fertiliser nitrogen applications of 120 kg/ha at sowing in the form of (a) ammonium sulphate and (b) ammonium nitrate, Treaton 1990

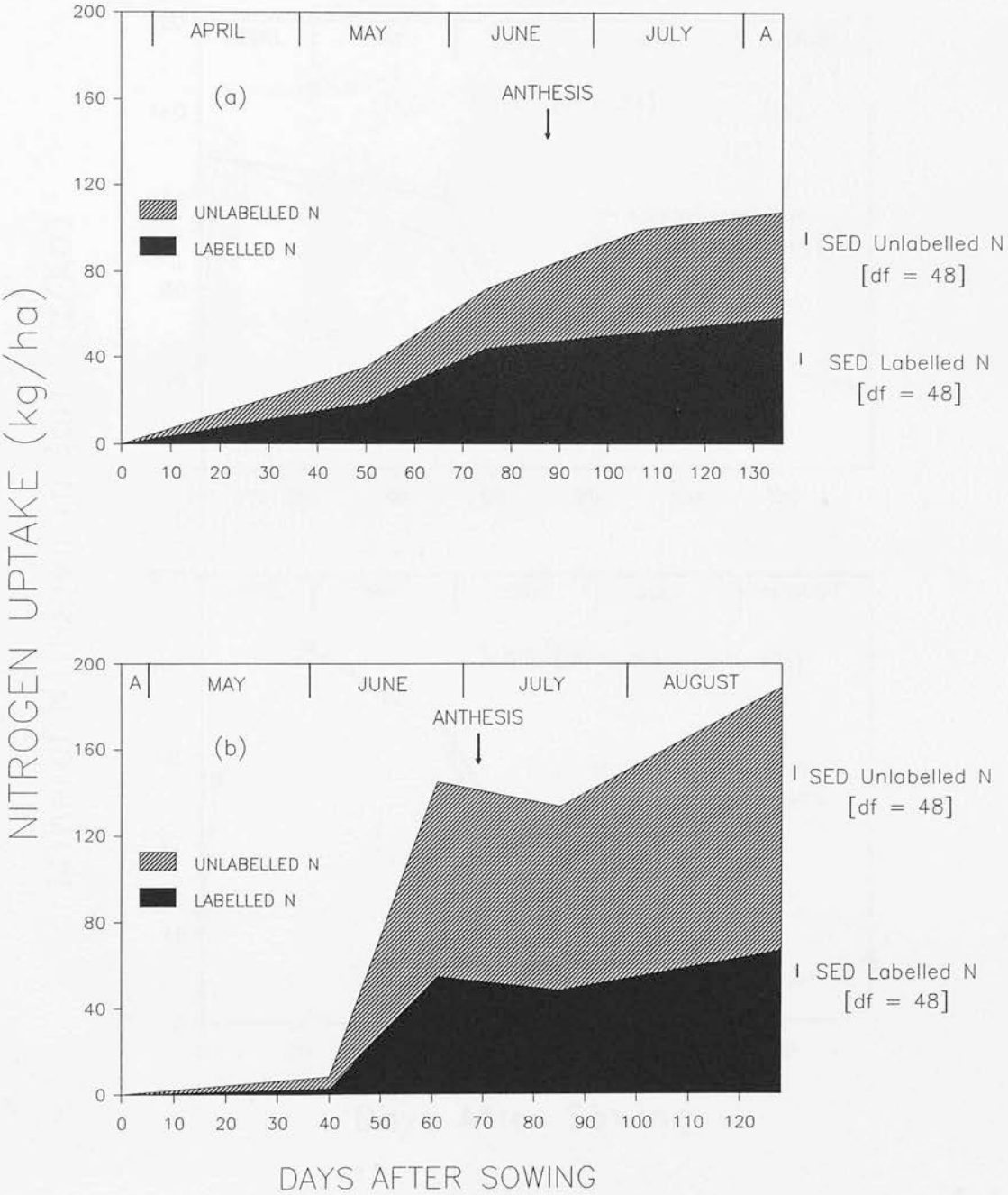

Figure A19. Uptake of labelled and unlabelled nitrogen over the growing season in spring barley after ammonium sulphate fertiliser applications of 120 kg N/ha at sowing (a) Manorhill 1990 and (b) Kettle 1990

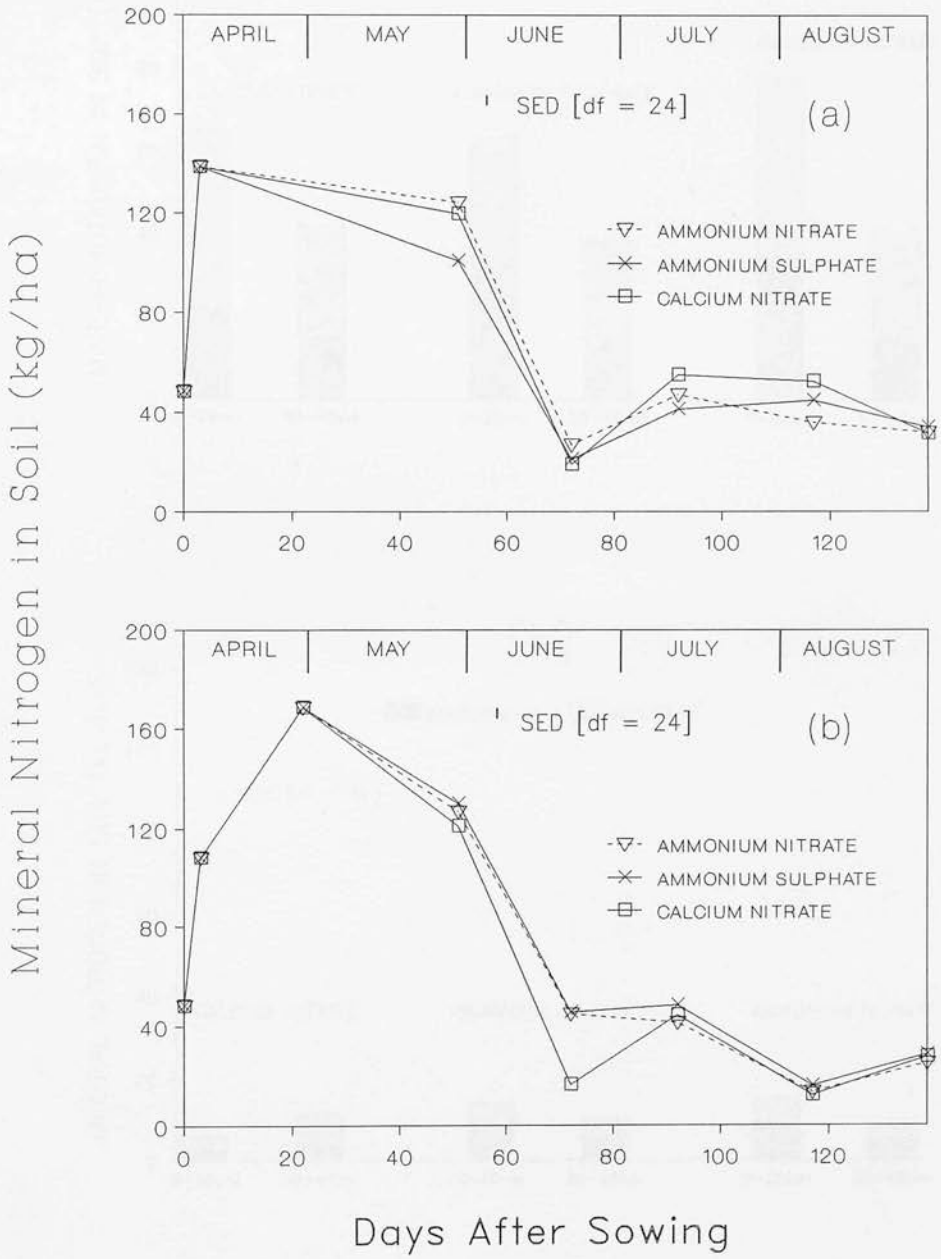

Figure A20. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley, with fertiliser nitrogen applied (a) 90 kg/ha at sowing and (b) 60 kg/ha at sowing and 60 kg/ha at emergence, Bush (Lower Fulford) 1988

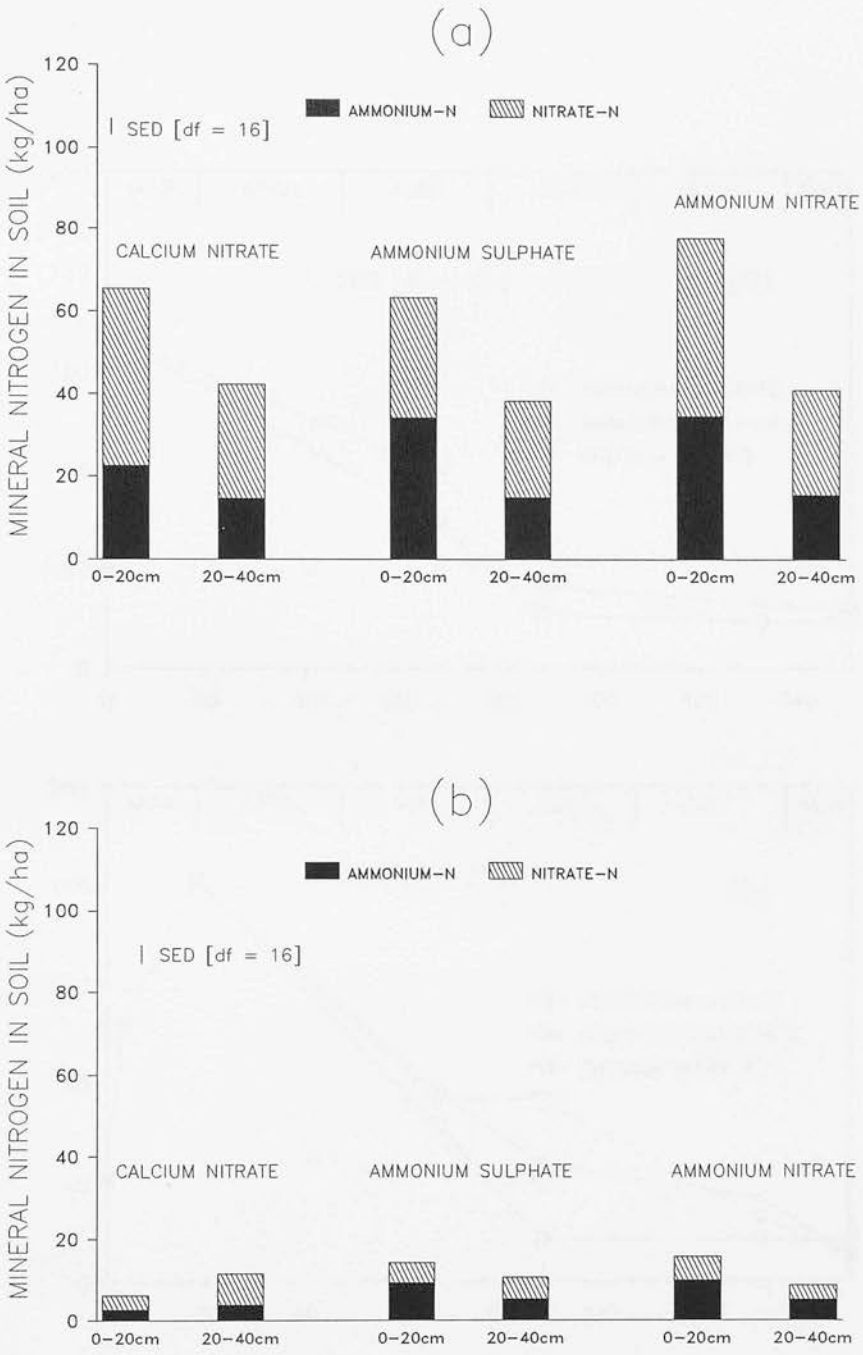

Figure A21. Quantities of nitrate- and ammonium-N at different depths in the soil at first two sampling dates, under spring barley fertilised with 120 kg/ha N fertiliser at sowing, (a) after 51 days (b) after 72 days, Bush (Lower Fulford) 1988

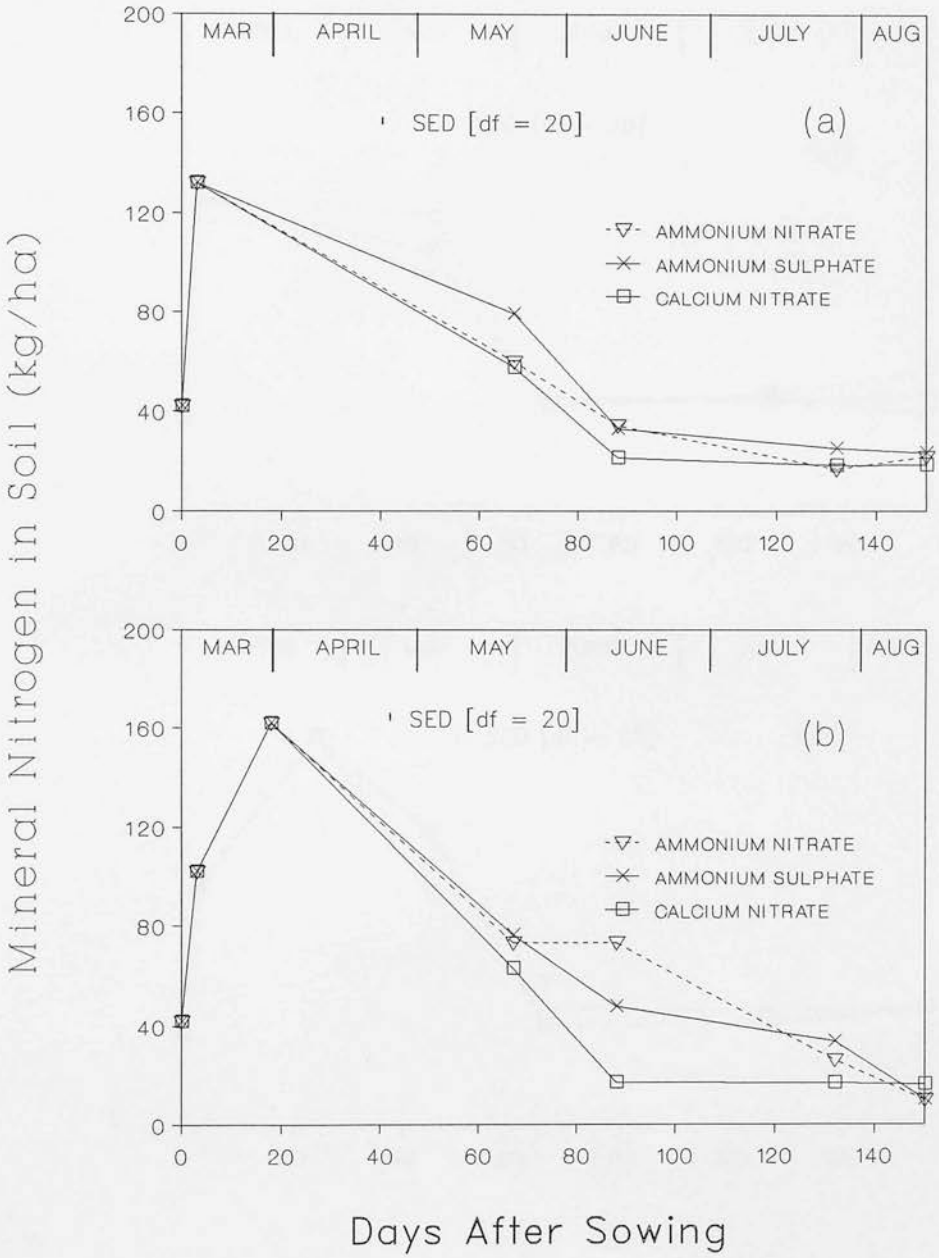

Figure A22. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley, with fertiliser nitrogen applied (a) 90 kg/ha at sowing and (b) 60 kg/ha at sowing and 60 kg/ha at emergence, Middlestot 1988

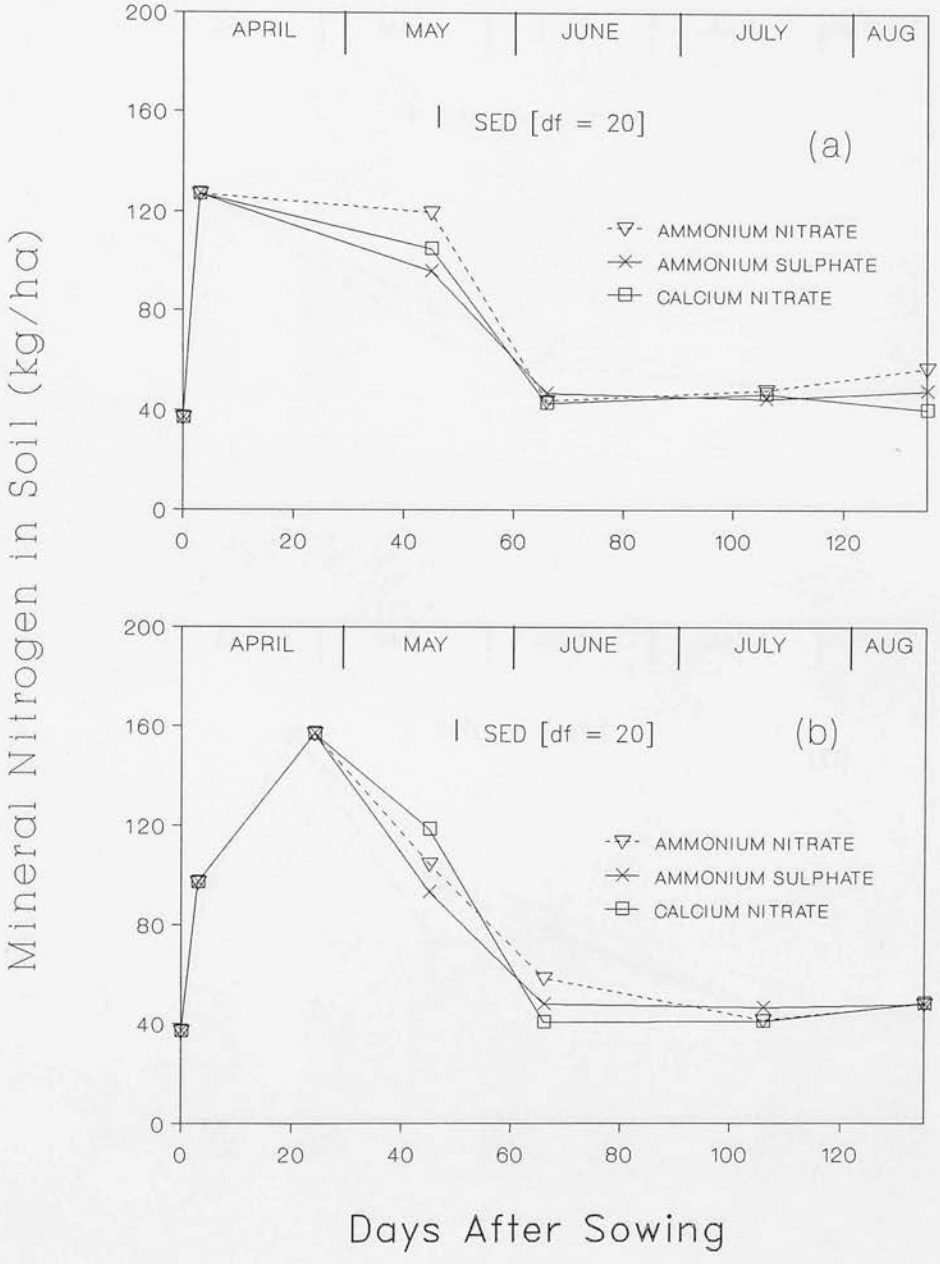

Figure A23. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley, with fertiliser nitrogen applied (a) 90 kg/ha at sowing and (b) 60 kg/ha at sowing and 60 kg/ha at emergence, Bush (March Park) 1989

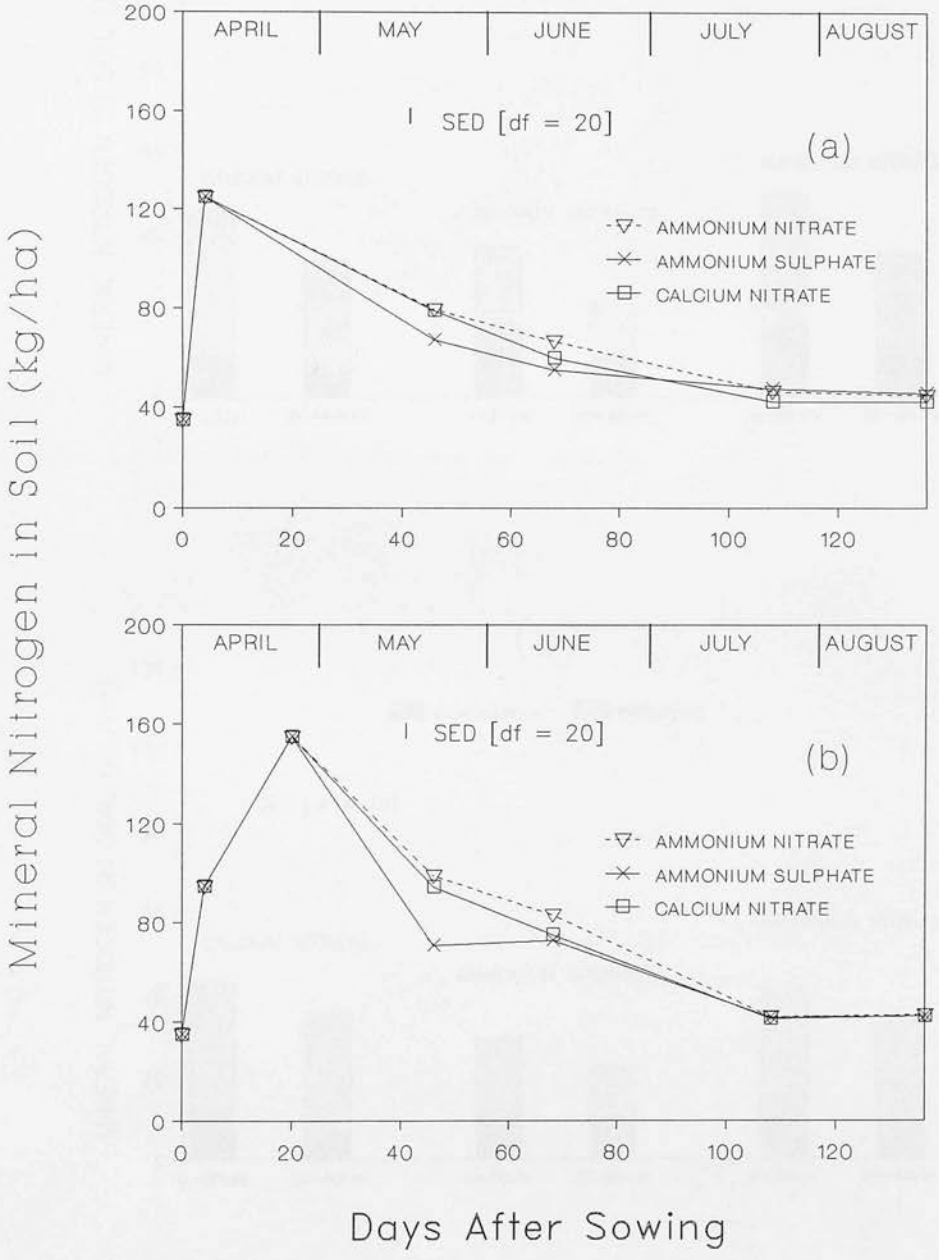

Figure A24. Changes in mineral nitrogen in the soil (0-40 cm) over the growing season, under spring barley, with fertiliser nitrogen applied (a) 90 kg/ha at sowing and (b) 60 kg/ha at sowing and 60 kg/ha at emergence, Upper Cairnie 1989

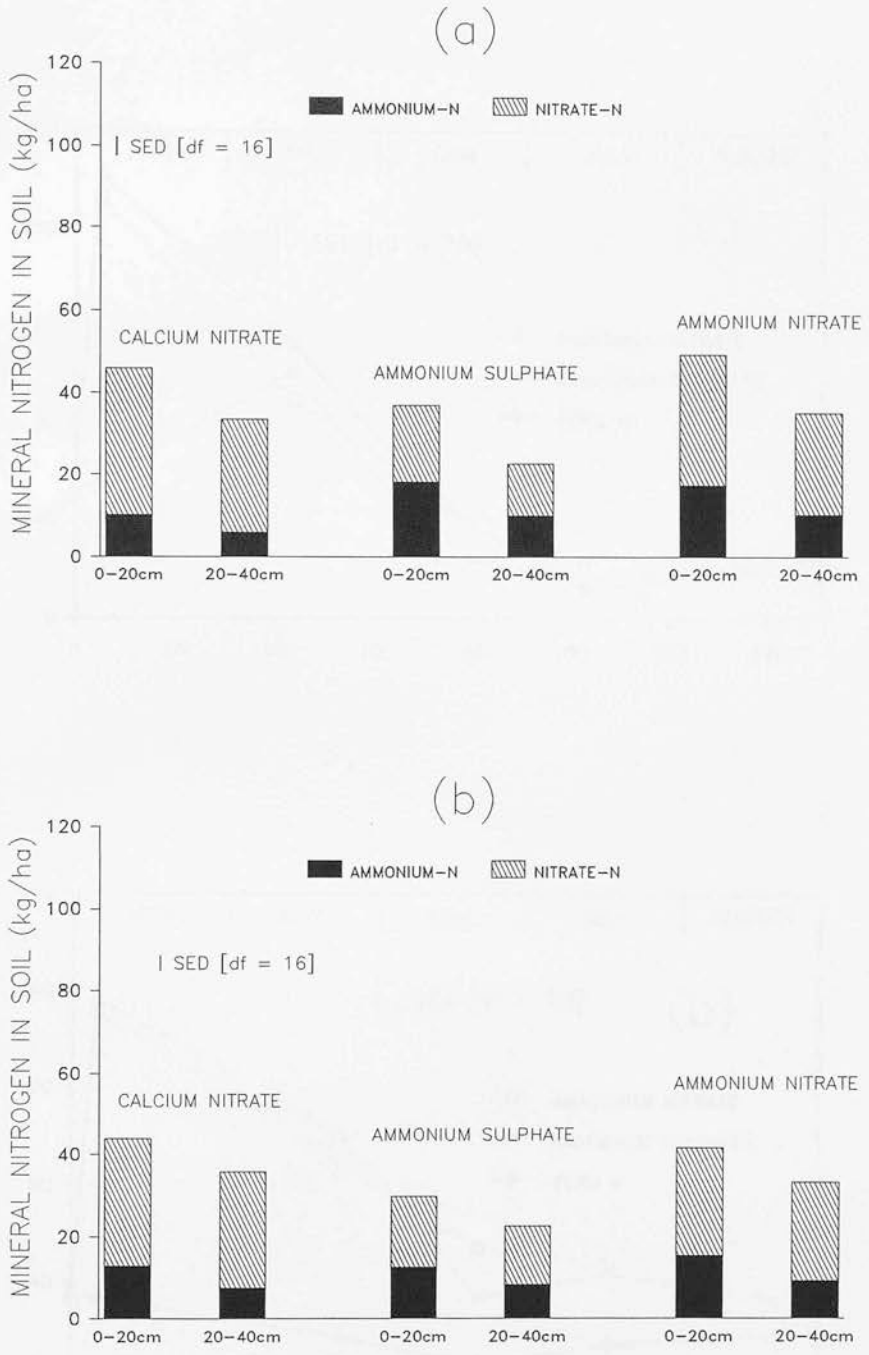

Figure A25. Quantities of nitrate- and ammonium-N at different depths in the soil at first two sampling dates, under spring barley fertilised with 120 kg/ha N fertiliser at sowing, (a) after 48 days (b) after 68 days, Upper Cairnie 1989

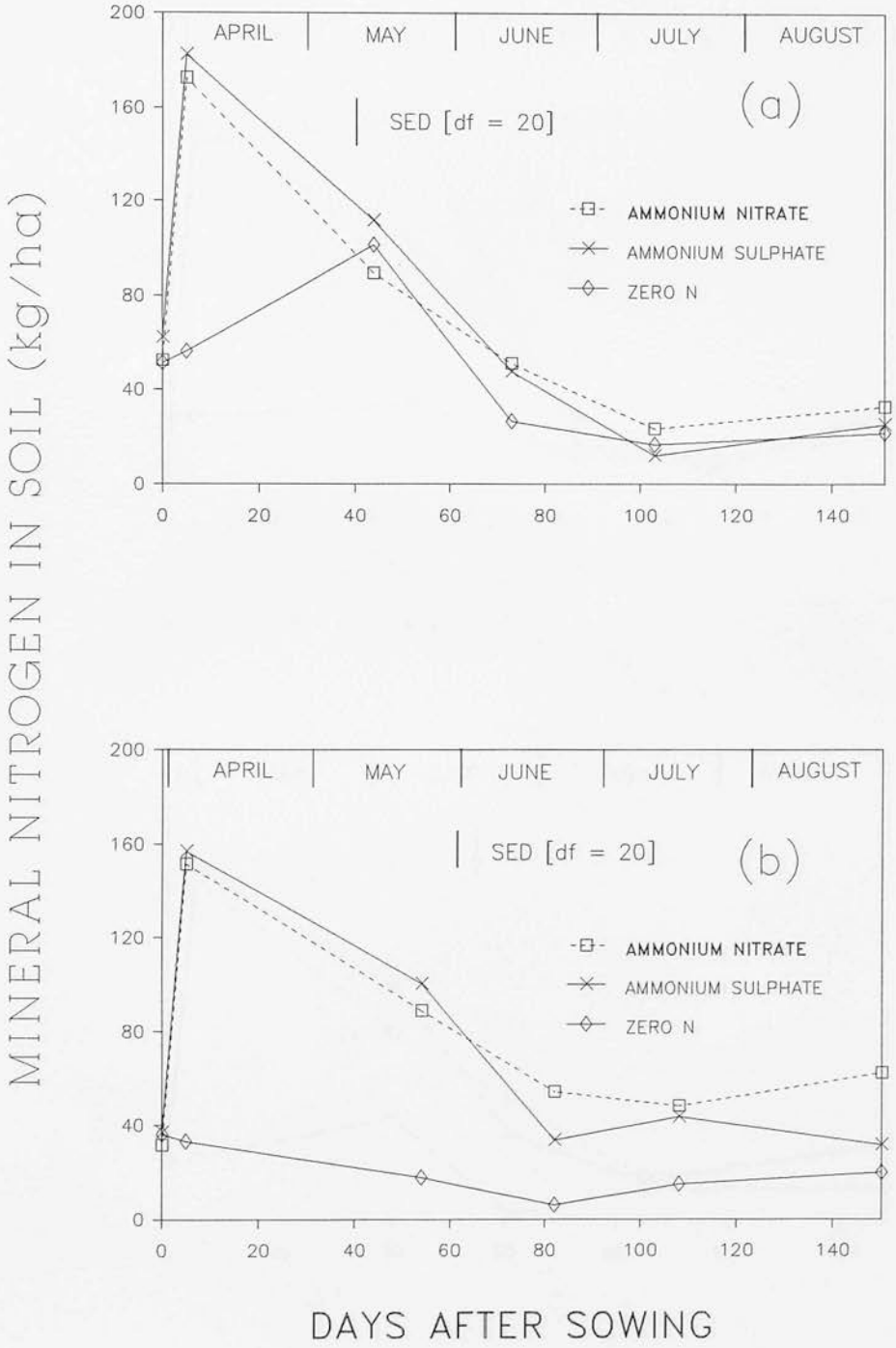

Figure A26. Changes in mineral nitrogen in the soil (0-30 cm) over the growing season, under spring barley, grown with zero or 120 kg/ha fertiliser nitrogen applied at sowing (a) Quixwood and (b) Bush (Crofts), 1990

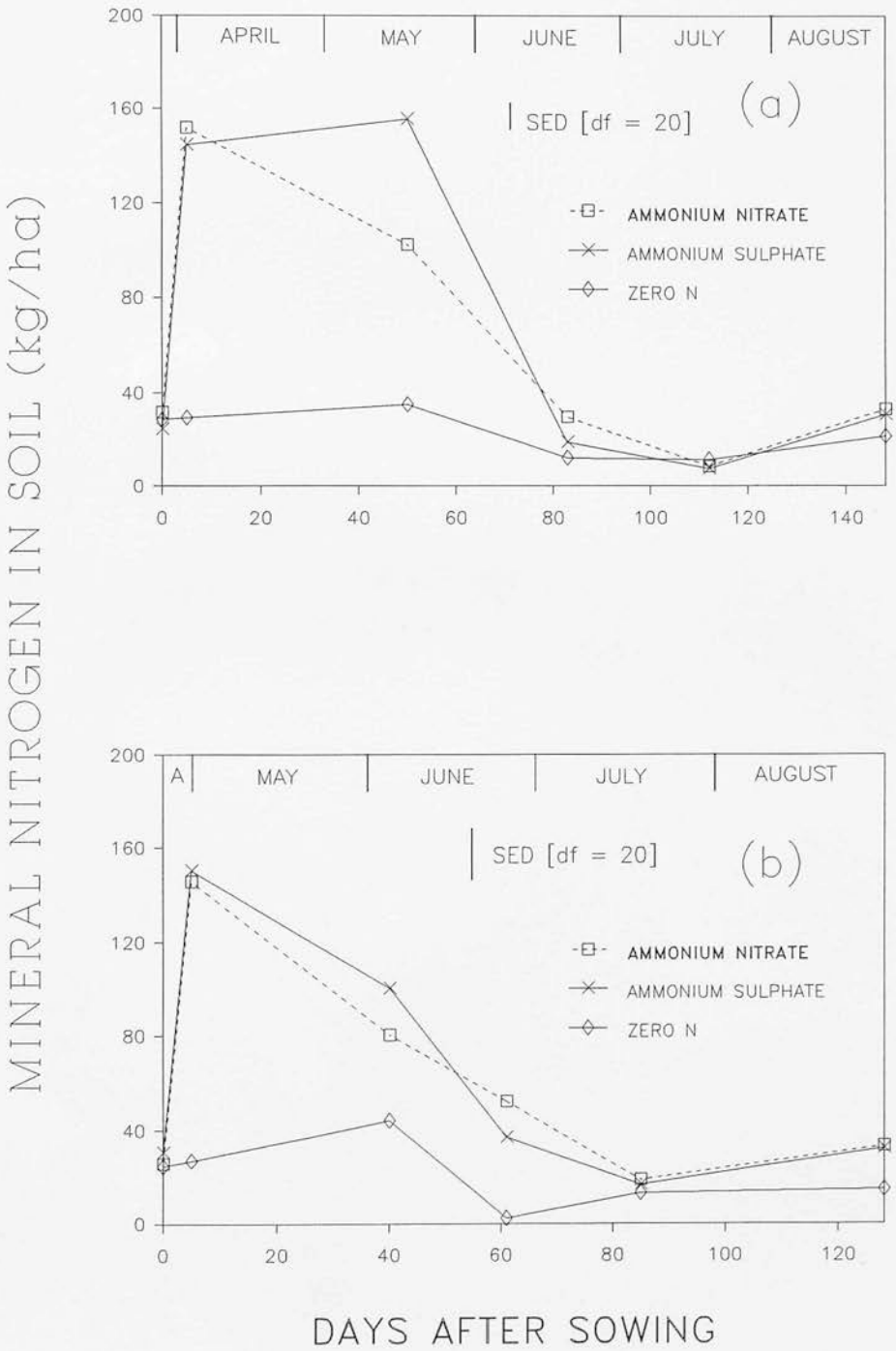

Figure A27. Changes in mineral nitrogen in the soil (0-30 cm) over the growing season, under spring barley, grown with zero or 120 kg/ha fertiliser nitrogen applied at sowing (a) Treaton and (b) Kettle, 1990